

Fifth International Conference on Frontiers of Polymers and Advanced Materials



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NATO Advanced Research Workshop on Polymers and Composites for Special Applications



BOOK OF ABSTRACTS

Organized By: Institute of Natural Fibres, Poznań, Poland
State University of New York (SUNY), Buffalo, USA
LETI - CEA (Technologies Avancées), Saclay, France

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**Fifth International Conference on Frontiers
of Polymers and Advanced Materials**



**NATO Advanced Research Workshop
Polymers and Composites for Special Applications**



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Institute of Natural Fibres
(INF)
Poznań, Poland



State University
of New York (SUNY)
Buffalo, USA



LETI – CEA
(Technologies Avancées)
Saclay, France

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MESSAGE FROM THE INTERNATIONAL CHAIRPERSON



I am pleased to welcome you to the 5th International Conference on Frontiers of Polymers and Advanced Materials and NATO Advanced Research Workshop on Polymers and Composites for Special Applications; The ICFPAM which is the fifth sequel of the highly successful ICFPAM and the NATO ARW, together, provides a unique opportunity to discuss current development with internationally recognized professionals, not only at the technical seminars but also in the casual atmosphere of the conference site.

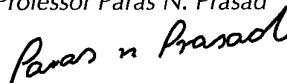
As we approach the next millenium, new technology will play an even bigger role in our daily life. The successful implementation of these technologies will be crucially dependent on availability of advanced materials. This conference focuses on both new technologies such as photonics, biophotonics and biotechnology as well as on new generation materials such as natural composites, environmentally friendly materials, nanostructured materials, inorganic-hybrids, biocomposites and biomimicry. The present conference focuses on these technologies and these classes of materials.

This conference deals not only with specific scientific developments, but the impact these materials have on the global economy. It also provides a unique scope involving a blend of science, technology and business by bringing together international scientists, engineers and top level industrial participants to discuss advances and new findings in polymers and advanced materials and their impact on new technologies.

We chose Poland as our conference site because of its long tradition of excellent scientific research in new materials, natural fibers as well as in polymers and composite materials. Poznań is the home of the Institute of Natural Fibers whose mission is to develop strong linkages between Research and Development centers, universities and industries.

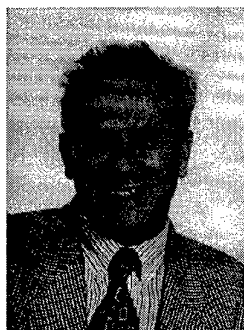
I owe gratitude to the National Chair for his leadership in the planning of this meeting. I thank the Conference Secretariat for its dedicated hard work in the organization of this Conference and the National Organizing Committee for its invaluable assistance. My sincere thanks are also to the International Co-ordinator, the Co-chairs, the Advisory Committee and the International Program Committee members as well as to all the symposium Chairpersons for their commitment over the last year.

Professor Paras N. Prasad



Director, Photonics Research Lab.,
State University of New York
Buffalo, NY, USA

MESSAGE FROM THE NATIONAL CHAIRPERSON



It is a great honor to Poland, Wielkopolska region and the city of Poznań to organize, in collaboration with the State University of New York at Buffalo, LETI-CEA Technologies Avancées and outstanding researchers from different countries, the Fifth International Conference on Frontiers of Polymers and Advanced Materials, held under the auspices of NATO and the State Committee for Scientific Research of the Republic of Poland. The fact that our meeting combines two conferences: the Fifth ICFPAM and NATO ARW on Polymers and Composites for Special Applications makes our honor even greater.

It is worth noticing that our meeting takes place in the year of the fiftieth anniversary of NATO which was marked by the admission of three nations of the former communist block to the structures of this Organization. In addition to this event of importance to the whole world, in Poland, and in Wielkopolska and Poznań in particular, we commemorate the anniversary of so-called Poznań June '56, which was one of the first rebellions against communist oppression in Central and Eastern Europe. Today, after fifty years, we can look ahead with optimism and faith in the victory for truth and justice. The participation of representatives of so many nations of the world in our conferences indicates our firm belief that the collaboration in the field of science and technology on the verge of the new millenium can result in prosperity for the whole world.

As I have already mentioned, leaders of the world science in five very important fields: natural fibers and composites based on them, nanostructured materials, materials for electronics and photonics, inorganic-organic hybrid composites and biomimicry, have contributed to our Conference and their presence will ensure the success of the conference. The presence of outstanding representatives of economic circles, the press, radio and television adds splendor to our Conference and shows that it holds much interest for the society.

At the end I would like to mention that the Conference is also a great event for the Institute of Natural Fibres and our contribution to its organization is one of the crowning achievements of our 70-year long activities in the field of natural textile raw materials. Let our Conference will challenge us to coexistence and competition for better quality, friendliness to the environment and to economic collaboration.

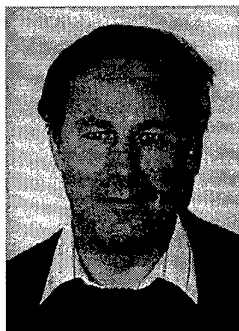
I wish to express my gratitude and the greatest respect to all people of good will who contributed to the organization of this Conference at the Institute of Natural Fibres, and in particular to the International Chairperson - the founder of the ICFPAM and International Coordinator for his inspiring leadership and great deal of effort made while preparing our Conference.

I would like to assure you that we will do our best to convince the participants of the Conference that Poland deserved its organization and the admission to the powerful defense Organization of free nations of the world.

Professor Dr. Ryszard Kozłowski

Director Institute of Natural Fibres
Poznań, Poland

MESSAGE FROM THE INTERNATIONAL CO-ORDINATOR



I am particularly pleased that the 5th International Conference on Frontiers of Polymers and Advanced Materials combined with the NATO Advanced Research Workshop on Polymers and Composites for Special Applications takes place in Poland, in the old and beautiful city of Poznań, known not only as the cradle of Polish State and the host of International Trade Fairs but also for its excellent scientific research. Poznań is the hometown of the well reputed Adam Mickiewicz University, several excellent technical universities, research laboratories with some of them active in the field of polymers and advanced polymers. The host institution - Institute of Natural Fibers, created in 1930, made his international reputation on important, original research on natural fibers and their application in the current human life.

We are delighted by the wide international attendance to this Conference. Participants from more than 30 countries, coming from six continents will be present. As in preceding conferences the meetings will start with general plenary talks, common for all attendees, followed by five specialized parallel sessions on:

- Natural Fibres, Composites and Environmentally Friendly Materials*
- Nanostructured Materials, Nanoparticles and Nanocomposites*
- Polymeric Materials and Composites for Electronics and Photonics*
- Inorganic - Organic Hybrid Composites*
- Biocomposites and Biomimicry*

Each session starts with invited talks, given by leading scientists in corresponding research fields, followed by shorter oral contributions on most recent achievements. Two poster sessions are also organized, which will provide a forum for discussion and interaction between the conference participants. The long coffee breaks as well as meals will provide the same opportunities.

I would like to express my gratitude to the conference chairs and co-chairs, the chairs of different symposia as well as the chairs and members of National Organizing Committee, International Advisory Committee and International Program Committee for all suggestions and help they provided for the organization of this conference. My particular thanks are due to the members of the Conference Secretariat for the invaluable and hard work they have done in managing in a beautiful way different practical and organizational as well as scientific aspects of the Conference. Special thanks are also due to the conference sponsors whose generosity was very helpful in the organization of this important meeting. I am looking forward to a very successful meeting.

Dr. François Kajzar


LETI - CEA, France

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Sunday, June 20, 1999

- 18:00 – 21:30 **Registration** (*Hotel Polonez*) and than since Monday at the conference site (*Institute of Natural Fibres*)
- 19:30 – 21:30 **Welcome Reception** (*Hotel Polonez*)

Monday, June 21, 1999

- 10:00 – 12:00 **Inaugural Ceremony** (*Opera House*)
- 10:00 – 11:15 Welcome Address
- 11:15 – 11:30 **Break**
- 11:30 – 12:00 Ballet Presentation by Poznan Opera Ensemble
- 12:00 – 12:30 **Transportation to the Conference Site** (*Institute of Natural Fibers*)
- 12:30 – 14:00 **Lunch**

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Plenary Session

Plenary lecture

**US DEFENSE PROGRAMS FOR INTERNATIONAL
COLLABORATION**

Joyce L. Illinger, PhD
Director
European Research Office
223/231 Old Marylebone Road
London NW8 8QS, UK

The Research Departments of the United States Army, Navy and Air Force maintain offices located in London, UK. The mission of these offices is to maintain awareness of research being performed throughout all of Europe to include independent countries that were part of the Warsaw Pact and the Former Soviet Union. All three services are concerned to seek out overseas expertise that is different from and complementary to that of interest to each individual service. We are co-located at the same address and frequently share site visits and conference support. Each service approaches scientific cooperation through different programs.

The Army's European Research Office (ERO) employs six scientists with expertise in Materials Science, Chemistry & Biotechnology, Physics & Electronics, Aeronautics & Mechanics, Human Sciences, and Environmental Science. We are interested in basic research that can have an impact on Army needs. These needs include becoming lighter, more mobile, and more durable; requiring fewer supplies to maintain function; improving communication, data transmission, data storage, and data manipulation; and developing lighter longer lasting power supplies.

Our scientists visit Universities, Laboratories and Institutes for face to face discussions and exploration of capabilities of doing research of mutual interest. We support focussed conferences in Europe. We help support travel for visiting experts to U.S. Army Research Laboratories and Centers and Army sponsored conferences. We have a small program to support "seed" projects in the hopes of developing long-term collaborative research and partnerships.

Plenary lecture

HIGHER EDUCATION AND INTERNATIONAL COLLABORATION

K. Grant

Dean, University of Buffalo, USA

Plenary lecture

**EFFECTS OF OPTICAL LIMITATION IN ORGANIC MOLECULES
AND COMPOSITE MATERIALS**

F. Micheron
Scientific Director
Thomson CSF, France

The need for optical limiters arises from the requirements of protecting the optical imaging devices, including the eyes, from laser aggression. Complex organic molecules in solvents are ideal systems for tailoring non linear optical properties of an optical cell included in the optical system, designed to protect the imaging device located at the focal plane.

Practical optical cells would need solid materials instead of liquids; therefore a lot of effort has been devoted to include these organic molecules inside solid matrices such as polymers and inorganic glasses. Since some interactions may be observed between the two phases of such composite materials, other approaches are now considered for optical limiting which use such interactions as the basic non-linear optical effect.

For instance, Carbon or polymer particles in suspension in liquids are investigated, which provide excellent results; more over, the concept of transparent composite materials in which optical scattering can be photo induced by changing the refractive index of one of the two phases will be presented and discussed.

Plenary lecture

**BIO-BASED RESOURCES IN THE 21ST CENTURY: DEVELOPING
THE INFRASTRUCTURE TO MEET THE DEMAND**

F.A. Riccio, Jr.

President

Danforth International Trade Associates, USA

Science and technology continues to make significant inroads in the potential use of these resources and industry's interest is growing. With the exception of the forest products sector there are no systems for the production and/or collection, processing and delivery of these materials to the markets. Evidence suggests that nonwoods from agricultural residues, natural stands, dedicated crops, etc. will be required to fill increasing demand as our wood resources may be over taxed.

Plenary lecture

**ELEMENTS PERIODICAL SYSTEM – THE BASE OF EXTREMAL
PROPERTIES PROGNOSIS AND NEW HIGH – PERFORMANCE
ORIENTED MATERIALS (FIBRES, WHISKERS) CREATION.
THEORY, PRACTICE AND PERSPECTIVE**

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There are great achievements in the area of extremal mechanical and thermal properties materials creation, including fibres, films and whiskers. The problem of *дальней* properties (theoretical and limited attainable strength, modulus and thermal stability) for these has the great scientific significance as well as practical discovering of real materials with maximal properties values.

Just therefore are arising the following questions: "What are the limits of materials properties?" "What kind of material must will have limited, the most high properties among elements and compounds thinkable on the base of Periodical System of D. I. Mendeleev?" "What ways are optimal for further achievements in area of high-performance materials?" During time these interesting low-investigated questions converted to one of important theoretical problem of solid physics and mechanics for anisotropic polymeric materials: fibres, films, whiskers, as well as practical discovering of real materials with maximal properties values.

More than 45 years theoretical and 30-years practical experience in this field help me to answer these questions. There were created the complex of scientific foundations and developed practical researches in these important directions. In paper is presented today state of limited mechanical and thermal properties problem of fibres, films and whiskers for different purposes, including authors long time investigations.

Many years author elaborated different independent methods for determination of theoretical and limited attainable strength and modulus by structural mechanics methods. The new important for practic characteristics - limited attainable properties were suggested for defectless ideal crystalline materials (at assigned temperature - time $T - \tau$ conditions) in contrary to theoretical properties (at absolute zero temperature $T \rightarrow 0$ K by H. Mark, G. Bartenev). Two new indexes - intermolecular and interatomic energy density were suggested too, which are important for mechanical properties prognosis.

Chemical bonds energy density and extremal properties for many elements and compounds of D. I. Mendeleev Periodical System were calculated and examined. The substances of linear and layer structures with maximal chemical bonds energy density were marked. The same calculations were done for all main linear oriented polymeric fibres. Many of results are the first in scientific literature. The extremal properties calculations were done with two independent methods and controlled by some experimental physical methods.

Comparative analysis of specific (related to mass or volume unit) interatomic interactions energies for different substances show, that maximal energy density have "light" 3-d and 4-th valence elements of Periodical System 2-nd and 3-d groups and their compounds - carbides, nitrides, oxides. This substances may-be the materials with the most high properties. Oriented polymeric materials (fibres, whiskers) belong to this group too.

The oriented polymeric materials with maximal theoretical and limited obtainable properties are determined. That are linear carbon polymer β -carbine as the most high modulus and the most strong material in Nature. Not far of that are hexagonal structures - boron nitride, graphite and silicon carbide. The most thermal stable among polymeric materials is graphite, that is confirmed by fulfilled calculations and corresponded to experimental results

The theoretical and limited attainable elasticity modulus and strength as well as limited thermal stability properties of many ordinary and especially high performance fibres were calculated by different independent methods on the base of ideal crystal model of linear (aliphatic and aromatic) and layer structures. The results are correlated with interatomic chemical bonds energy density in axial direction. Many of results were the first in scientific literature, for example for β - carbine and para-aramides. A part of literature data were corrected and completed too.

There were analyzed aliphatic and aromatic including para-aramide carbocyclic and heterocyclic polymers and fibres; their theoretical and limited attainable mechanical properties in comparison with maximal real indexes. The same was done for carbon fibres. There were introduced new indexes – structural perfection coefficients, which are characterized integral perfection of production method. All these calculations permit to know the principal possibility for arising properties to day produced and new high-performance materials.

Very interesting practical investigations to achievement of maximal mechanical properties fibres on the basis of rigid-chain and layer polymers have been done.

Practical investigations were compared with calculation results for achievement of polymeric fibres maximal properties and discussed from thermodynamic and kinetic point of view. There is a difference between thermodynamic and kinetic requirements for achievement of structure maximum regularity and maximal properties approach. Therefore the ideal molecular structure must be corrected for regulation of kinetical flexibility in fibreforming processes and fibres treatments. The main principles of high-performance fibres structure and properties regulations are discussed.

Today oriented PBZ - structures (poly-p-phenylene-bis-benzothiazol and -oxazol) are the most perspective as real fibres with extremal mechanical and thermal properties among linear polymers and carbon graphite structure among layer polymers.

All mentioned above calculations and examinations results of limited properties can (or must) be used to the prediction of most perspective oriented polymeric materials (especially fibres, films and whiskers) and ways for practical achievement of maximal properties values.

Prof. Herman Mark (Brooklin Polytechnical Institute) has given me the first impulse for this "hobby - work" in the time of my studying in higher school and later. His attention, the discussion contacts with him and my teacher Prof. Alexander A. Meos of studying period in St-Petersburg State University of technology and Design (former Leningrad Textile Institute) helped me a lot. Therefore this paper is devoted to the memory of Prof. H. Mark and Prof. A. I. Meos.

FIBERS FOR THE NEXT MILLENNIUM

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As we enter 21st century technical advances are dramatically influencing the world of fibers, fabrics and textiles. Today, technology can provide us with fabrics that imitate and actually improve upon nature's best fibers. In the next millennium, textiles will not just be an extension or simple alternatives to natural or synthetic fibers, but will provide superior aesthetics and functionality in broad and emerging sectors of the economy from space to super conductivity and agriculture to geotextile. This will be accomplished through low cost petroleum based feedstocks, highly efficient production schemes with no adverse impact on the environment, and ease of care and durability of products. It is suggested that developments in materials, information and biological sciences will figure prominently in the development of tomorrow's textiles.

Natural Fibres, Composites and Environmentally Friendly Materials

Invited lecture

INVENTORY OF WORLD FIBERS AND INVOLVEMENT OF FAO IN FIBRE RESEARCH

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There is a greater awareness of need for fibers and materials in a world of expanding population and increasing affluence. The general classification of fibers recognizes natural and chemical (man-made fibers). The detailed classification is described in a table. The natural fibers are divided into animal, vegetable and mineral. The present world inventory of fibers is estimated at 54.2 million tons (100%) and the share of major classes of fibers is as follows: cotton 19.02 million tons (35.1%); man-made fibers 28.18 million tons (PES, PAC, PA 43.3%; PP 8.7%); wool 2.01 million tons (3.7%); and other natural fibers 4.99 million tons (9.2%). The inventory of major potential world fibrous raw materials from agricultural crops is estimated at ca 2,510,400 thousand tons and it is growing. The natural fibers inventory, including wood resources and natural cellulosic fibers, consists of the following resources: wood, straw (wheat, rice, oats, barley, rye, oil flax), grass e. g. esparto and sabai grass, stalks (corn, sorghum, cotton), bagasse, reeds, bamboo, cotton staple, core (jute, kenaf, hemp), bast (jute, kenaf, hemp, ramie), papyrus, cotton linters, leaf (sisal, abaca, henequen), and other hard fibers: coir, caroa, cabuya, letona, maguey, banana, doum and aloe.

We are interested in green fibers, such as: flax, hemp, ramie, jute, sisal, coir, abaca, henequen, curaua etc. They are produced by nature in lavish abundance. The giant chemical companies have recognized this and are changing into „agrobusinesses”. Biomass, including these green fibers, can be produced everyday, everywhere, neither causing pollution nor disturbing the CO₂ balance of our planet. In textiles, the share of clean, biodegradable cellulosic fibers in world fiber production is about 50% and is decreasing due to fierce competition between natural and synthetic textile polymers. Among man-made fibers we can distinguish fibers which have new, unconventional characteristics as „functional fibers”. They are products of advanced high technology, having superb strength, high elasticity and great heat resistance. Most authors discuss totally aromatic polyamides (aramid), totally aromatic polyesters (polyarylate), ultra-high molecular weight polyethylene, phenol fibers, carbon fibers, silicon carbide fibers, alumina fibers, ceramic fibers and whiskers etc.

Taking into consideration the special properties of functional fibers the author describes features of the following fibers: electric anti-static, electric conductive, flame retardant and flame proof, ultraviolet light reducing fibers (ultraviolet shielding fibers), insect-free and mite-repellent fibers, anti-bacterial and odor-preventing fibers, deodorizing fibers, shingosen (finely textured fibre). The role and importance of chemical fibers and those obtained from natural polymers is increasing. The world is looking forward to the new

chemical fibers and their applications, as well as to the natural fibers obtained using biotechnological methods (e.g. biosilk).

The traditional application of man-made and natural fibers is, of course, in the textile and apparel sectors, but we notice an increasing importance of non-textile applications of lignocellulosic bio-composites in new, emerging and promising areas of usage such as: geotextiles, chemo-textiles, grass mats (reinforcement of slopes and embankments), particleboards, filters, pulp, bio-composites applied in furniture industry, transport industry etc. It is possible to make completely new types of composite materials based on fibers by combining different resources. It is also possible to combine and blend lignocellulosic or agro-based fibers with materials such glass, metal, plastics and synthetics to produce new classes of composite materials. Some advantages of composites containing natural, vegetable fibers, as well as limitations of application of those fibers in composites are presented. The challenges in the competition between natural and man-made fibers are described.

At present, the world population grows at a rate of 1 billion people every eleven years. Between the years 1980-2050 world population is expected to increase from 3.7 to 11 billion people. It is obvious that the consumption and demand for wood and pulp will increase accordingly. Pulp production in the next 10 years has to grow from 270 to 480 million tons, according to the forecast regarding population growth and world pulp demand.

At the same time the request for supplies of fiber supporting the production and reinforcement of pulp will grow as well. It is remarkable that the forecasts predict that forest area (as a source of pulp and fiber) will decrease from 3.44 billion ha to 2.42 ha by the year 2050. It does not go unnoticed the destruction of forests, even Brazilian rainforest, where a total area just smaller than Belgium (ca 29,000 km²) was destroyed in 1995. Facing such deforestation, it is important to notice the growing role of alternative sources of pulp production. The author shows the characteristics of wood and nonwood fibers (alternative) for papermaking (e.g. nonwood plant fibers like grass, bast, leaf and fruit fibers; nonplant fibers from animals and minerals, and organic and inorganic man-made fibers etc.). A fierce competition between natural and other fibers is noticeable. An advisable solution is to find and introduce harmonious coexistence.

As the coordinator of the FAO European Cooperative Research Network on Flax and Other Bast Plants, acting within the FAO ESCORENA system (EUROPEAN SYSTEM OF COOPERATIVE RESEARCH NETWORKS IN AGRICULTURE), the author is going to present the FAO involvement in fiber research. The FAO Network on Flax and Other Bast Plants is acting simultaneously with other Networks on plants of such importance as: cotton, rice, soybeans, sunflower, olives, pasture and fodder crops.

The FAO in Rome is interested in promoting research cooperation and realizes FAO programs and initiatives for technical cooperation and partnership. Within the FAO act the Intergovernmental Group on Hard Fibres and the Intergovernmental Group on Jute, Kenaf and Allied Fibres. These groups conduct fiber research in the scope of the above mentioned fibers, organize meetings, consultations, discussion and provide relevant statistical data.

The FAO promotes the research cooperation and exchange of information through: holding conferences, as well as through newsletters, publications, proceedings of the research events. The FAO also promotes the transfer of know-how and methodology advances, with clear sustainable development and socio-economic implications under the umbrella of the ESCORENA System.

Invited lecture

**NONWOOD CELLULOSE FIBERS IN ADVANCED MATERIALS;
INDUSTRIAL DEVELOPMENT AND BUSINESS OPPORTUNITIES**

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Whether it's for reasons of environmental compatibility, alternative/sustainable agricultural development or the potential enhancement of the physical properties of a given product, we've been witnessing increased interest in the use of nonwood cellulose fibers in both traditional and emerging industrial technologies.

Government and academic research has led the way in accomplishing essential research in the area of cellulose fiber use in advanced composites and industry is now acknowledging the value of this work by exploring the potential opportunities in the technologies and materials.

Business and industry are ultimately faced with the task of determining the economic potential of new technologies, the feasibility of new or modified manufacturing methods and materials, the costs of a transition and the return on investment.

Industry requires a meaningful assessment of potential to determine the viability of any undertaking and this begins with defining true market demand, distinct from interest.

Both sides of the current equation must make these assessments. That is, fiber producers must define potential requirements to insure adequate materials and infrastructure and to justify their investments. Manufacturers, i.e., the consumers of these fibers, must define their requirements for specific fibers based on costs and performance needs, identify their markets and determine how they will respond in order to develop meaningful forecasts and discern the feasibility of their ventures.

This paper will explore the current status of available fibers and the infrastructures to support their delivery to industry, as well as the opportunities and obstacles facing industry in the implementation of new technologies and the use of alternative materials.

Invited lecture

PROBLEMS IN INDUSTRIAL USE OF PLANT FIBRES FOR MOULDED COMPOSITES

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Moulded composites based on plant fibres have so far only been a significant success within the automotive industry, although both designers and manufacturers have shown great interest in using a renewable resource for the production of three-dimensional products. A major problem is the procurement of suitable plant fibre-based mats for hot pressing. Most of the existing plant fibre-based mats are made for the automotive industry, and after hot pressing these provide a product with a rather rough surface that is not suitable for painting. If an industry obtains a small matforming machine for the manufacture of suitable mats, where does this industry get the required volumen and quality of fibres? In addition, moulds may be very expensive and thus only economical for mass production.

A lot of research has been and is continuing to be undertaken. However, if we wish to see the result of this effort, more work has to be done in solving the above-mentioned problems. This is not a question about research but about organization. Most likely all the know-how exists, but how do we combine this, in such a way that an interested manufacturer can get started with the production of these new three-dimensional, plant fibre-based composites, which we all believe have a great future. How do we supply small and medium sized enterprises with some tens or hundreds of tons of suitable mats per year for the production of furniture, loudspeakers, bus seats, etc? Apart from the automotive industry we have not been able to convince economically strong industries about the potential of plant fibres for the manufacture of three-dimensional products. A solution to these problems is the way to enhance the industrial use of plant fibres in the near future.

Invited lecture

CHEMICAL AND THERMAL CHARACTERIZATION OF CURAUA FIBER

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This paper describes the chemical, thermal and thermomechanical characterization of curaua fiber. The research of the thermal and thermomechanical properties of natural fibers is of major interest, considering their increasing utilization in several applications, and the large temperature range to which the fibers are submitted. Natural fibers, especially curaua, have some outstanding properties so that these fibers can be used for application besides the traditional fibers (rami, sisal, and jute).

Curaua - *Ananas erectifolius* - This is a hydrophilous species from the Amazon region. Its leaves are hard, erect and have flat surfaces. The leaves are about one meter long, or more, and 4 cm wide. The plant requires 2,000 mm or more of annual precipitation, preferring silil-humus soils, but also grows in clay-silic soils. Indians commonly use it for hammocks and fishing lines. Eight months old leaves can reach up 1.5m in length, and 50-60 leaves per year. The dry fiber content in leaves is about 5-8%. The fiber is commonly extracted by a primitive process called "forca" (hanger), washed and beaten with a circular rod and left in water in order to mercerize for 36 hours. They are again washed and allowed to dry. Curaua is very competitive among the traditional fibers, always ranking in the top three for economical analysis and top four for stiffness [1]. The thermal behavior study was performed using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) techniques, between 18°C and 600°C, -50°C and 300°C, respectively, for 10°/min heating rate under air atmospheres.

Of the curve corresponding to DSC of the curauá fiber, was observed that, a endothermic peak in approximately 173°C that can be associated the occurrence of the rupture of inter and intramoleculares linkages. Around to 270°C an endothermic peak is observed regarding the beginning of the degradation of the cellulose.

TG was used to evaluate the alterations at level of thermal stability of the samples. The results of the analyses obtained for the curaua fiber showed loss of water and of some components up to 200°C; in the range above 250°C the beginning of the degradation of the chemistry structures of the components of the fibers followed by the carbonization, with loss of mass that vary of the range from 18 to 85%. Illustrations of the curves TG demonstrated that the limit for application of the fiber is around 225°C. Already, in the range of 250 to 400°C occurs the degradation of the cellulose [2].

Thermomechanical Analysis (TMA) have been used for evaluate the dimensional stability. of the natural fibers. The measurements were conducted in a helium atmosphere. The following temperature program was used at $-50 - 420^{\circ}\text{C}$, heating rate $5^{\circ}\text{C}/\text{min}$. For the measurements, a single fiber and in comparison eight (bundles) fibers were taken to place in the tension sample holder. The load amounted to 5 cN. The single fiber shows a thermomechanical effect at -15°C . The break onset is achieved at 315°C . In the bundle the change of expansion is missed at low temperature. Here a significant change can be observed at 220°C (onset). After another onset at 313°C , the expansion of the bundle reaches a maximum at 328°C before it drastically returns due to retraction. The break point of the bundle is at 376°C . Again the single fiber has a lower mechanical stability. Strong differences can be seen in the expansion coefficients (α). In the temperature range between -50°C to 20°C the bundles has an α of 10.57×10^{-6} while the single fiber shows an α of 38.07×10^{-6} due to big expansion at -15°C . The expansion coefficient between 20°C and the break point 328°C (bundle) respectively 325°C (single fiber) amounts to 43.41×10^{-6} for the bundle and 57.49×10^{-6} for the single fiber.

The curaua fibers were submitted to chemical analyses. It was analyzed by standard procedures (TAPPI)[3]. Degree of crystallinity values has been calculated by using the method described by Buschle-Diller and Zeronian [4]. The results of the chemical characterization and of the degree of crystallinity of the curaua fibers are summarized in the Table 1, in which the presence of a high cellulose content is verified.

Table 1: Chemical analyses and degree of crystallinity of curaua fibers (*water free).

Characteristics	%
Humidity	7.92
Ash *	0.79
Solubility hot water	1.03
Solubility NaOH 1%	19.3
Solubility cyclohexane:ethanol, 1:1*	0.48
Holocellulose *	91.8
Cellulose *	70.7
Klason Lignin *	11.1
Degree of Crystallinity	75.6

All these results showed that use of curaua fiber for composite materials or new products with new interesting properties is possible.

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Invited lecture

BIODEGRADABLE PLASTICS FROM CELLULOSE

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Cellulose acetates (CAs) comprise a class of commodity cellulose ester polymers that have been used widely for many decades. They also have been recognized to possess considerable biodegradability. Although CAs are well-known for their solubility in organic solvents, they lack of significant thermoplasticity. In an attempt to combine the positive attributes of CA with the attractive features of thermoplastic fatty polyesters (i.e., melt flow, biodegradability), reactions were explored in which a commercially available cellulose diacetate (CDA) was combined with dicarboxylic acid anhydrides and monoepoxides or polyols. The conditions chosen provide for flexibility so that a wide range of properties can be achieved. Biodegradability of the products was experimentally confirmed.

INTRODUCTION

A large number of interests have been occurring on biodegradable plastics. At present, investigations in the field of the bacterial producing polymers as well as the synthetic polymers are more actively and extensively pursued compared with the cases from natural origin polymers. However, it can be said as a whole, that the investigations on the biodegradable polymers have not reached to the stage of practical usages.

It is known that the biodegradable chemical intermonomer bonds include glycosides, peptides, and aliphatic esters¹. Thus, some of the most attractive materials with greatest potential in terms of cost, material applications, and environmental compatibility include cellulose derivatives, especially cellulose esters. Among the cellulose esters, cellulose acetate (CA) has been produced industrially in large amounts. Thus, the greatest interest has recently focussed on the potential biodegradability of CAs. Buchanan et al.² and Komarek et al.³ have demonstrated that CA with a degree of substitution (DS) of up to 2.5 can be degraded microbially. Sakai et al.⁴ have searched for fungi which decompose CAs, and they have demonstrated that *Neisseria sicca* can degrade CA with a DS of up to 2.3. It also has been suggested that CA would undergo an enzymatic splitting by acetyl esterase in a first stage, down to a DS of 1.0, before the degradation would continue by the action of cellulase enzymes³⁻⁵.

Since CA, including cellulose diacetate (CDA), has been recognized as a biodegradable polymer, various trials have been undertaken with the intent of imparting sufficient thermoplasticity to CAs in order to provide them with the melt-processability. This is

because CDA, which has the greatest thermoplasticity among all CAs, fails to show adequate melting behavior without decomposition or discoloring. Thus, reducing the flow temperature of CAs is important and it requires the addition of plasticizers and flow promoters.

Traditional plasticization of CAs has been accomplished using conventional plasticizers with low-molecular weights, such as diethyl phthalate, dibutyl phthalate, glyceryl triacetate, glyceryl tripropionate, triphenyl phosphate, tricresyl phosphate, and so forth. Especially, phthalates and phosphates are used industrially at present in procedures that are often very time-consuming (i.e., 4-5 hrs per batch). Use of these plasticizers are undesirable for the preparation of biodegradable polymers because of the harmful nature of the decomposition products. In this connection, there have been several attempts trying to utilize aliphatic polyesters as plasticizers for CAs.⁶⁾

In view of this situation, we have been attempting to find novel plasticizers and plasticizing procedures by which biodegradable thermoplastic polymers can be obtained from CAs.

EXPERIMENT

Oligoester chains were introduced into CDA (L-40; DS 2.45; Daicel Chemical Industries, LTD.) molecules by reacting CA with dicarboxylic acid anhydrides such as maleic anhydride (MA) and succinic anhydride (SA) together with monoepoxides such as phenyl glycidyl ether (PGE), styrene oxide (SO), and allyl glycidyl ether (AGE). The oligoesterifications of CAs have been carried out by the use of a compounding machine (Labo Plastomill LPM 18-125; Toyo-Seiki Co. Ltd.) at certain temperatures with constant kneading speed. Biodegradability of the oligoesterified CDAs was experimentally pursued by soil burial test at 30°C and 80 RH% and by measuring oxygen consumption in a closed activated sludge suspension.

RESULTS AND DISCUSSION

It was shown that cellulose diacetate (CDA) can be effectively plasticized by reactive melt-processing. To achieve effective plasticization, CDA must be graft-copolymerized with oligomers (i.e., internal plasticization). Cellulose triacetate, which does not have any residual hydroxyl groups and which has no possibility to be grafted, could not be plasticized by this method.

It was also shown that there often occurs a problem of (external) plasticizer bleeding. That is, homo-oligomers prepared during melt-processing are not stable in the moldings, tending to migrate from the inside to the surface. In this concern, direct evidence for the role of oligomer grafting onto CAs in preventing monomer and homo-oligomer bleeding was obtained experimentally. Cellulose monoacetate (CMA) more easily generates products with reduced bleeding compared to cellulose diacetate (CDA), supposedly because the grafting proceeds to a higher level in the former case.

The amount of grafting was intended to increase, by which the bleeding of monomers and homo-oligomers that had been formed during grafting could be effectively suppressed. From these findings, it appears the statement that the more effective grafting is attained, the more ideal plasticization of CA can be effectuated.

The plasticized CAs described above have been prepared by the use of reactive plasticizers which can be considered as biodegradable. Their preparation has also been based on the finding that CAs with a DS of up to 2.5 are biodegradable.^{2,3}) It was considered, however, that the biodegradability of modified CAs should be demonstrated experimentally. Thus, the soil burial tests in terms of changes in external appearance and changes in physical properties as well as the determination of the oxygen consumption within a closed activated sludge suspension were performed. As the results, the oligoester-grafted CAs were found to reveal distinct degradability. Overall, biodegradability was found to be affected by both amount and type of reactive plasticizer used.

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Invited lecture

EMERGING PLASTIC PRODUCTS FROM STARCH

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GENERAL

New environmental regulations, societal concerns, and a growing environmental awareness throughout the world have triggered the search for new products and processes that are compatible with the environment. Thus, new products have to be designed and engineered from cradle to grave incorporating a holistic "life cycle thinking" approach. The impact of raw material resources used in the manufacture of a product and the ultimate fate (disposal) of the product when it enters the waste stream have to be factored into the design of the product. The use of annually renewable resources and the biodegradability or recyclability of the product are becoming important design criteria. This has opened up new market opportunities for developing biodegradable products.

Currently, most products are designed with limited consideration of its ultimate disposability. Of particular concern are plastics used in single-use disposable packaging. Designing these materials to be biodegradable and ensuring that they end up in an appropriate disposal system is environmentally and ecologically sound. For example, by composting our biodegradable plastic and paper waste along with other "organic" compostable materials like yard, food, and agricultural wastes, we can generate much-needed carbon-rich compost (humic material). Compost amended soil has beneficial effects by increasing soil organic carbon, increasing water and nutrient retention, reducing chemical inputs, and suppressing plant disease. Composting infrastructures, so important for the use and disposal of biodegradable plastics, are growing in the U.S. and are in part being regulatory driven on the state level.

STARCH FOAM PRODUCTS

Naturally occurring biopolymers like starch and cellulose are readily biodegradable. Several companies are commercializing starch based thermoplastic technologies. Basically, these technologies involve thermoplasticization of the starch using water and heat under pressure. The starch is heated above the glass transition and melting temperature of its components. This results in disruption of the molecular structure resulting in a „destructurized starch” that has thermoplastic properties. A number of polymer compositions containing destructurized starch for different applications have been

described. However, products based solely on starch are extremely water sensitive and of limited utility. However, 90 to 99% starch, or very low ds (0.5, degree of substitution) hydroxy propylated starch, has found applications as loose-fill packaging material. They are offered as a biodegradable, water soluble, anti-static, environmentally friendly alternatives to expanded polystyrene (peanut packaging). The entire operation is carried out in a twin-screw extruder specially designed to hold the water (which functions as the plasticizer, and blowing agent). Additives such as poly(vinyl alcohol) (PVOH) and other similar compounds are added to the starch to improve processability. The resultant foam has the compressibility and resilience of polystyrene foam products. National Starch (through American Excelsior), Empak (a DuPont-Conagra joint venture), Novamont (Italy), Clean Green Packaging (Minnesota) are marketing loose-fill packaging products.

This year, a Michigan based small business, **KTM** Industries, has cleverly exploited the light-weight, non-toxic, water wettable adhesive property of extrusion foamed starch to produce a new family of products for children. The first product is a multi-colored foamed building block that is marketed under the brand name „**Wet N' Set Magic Nuudles**”. Within the next three months, this product will be marketed in approximately 500 stores in all 50 States, and in Europe, (visit web site www.wetnset.com). This is expected to expand to 1200 stores within a year

STARCH ESTERS

Modification of the starch -OH groups by esterification chemistry to form starch esters of appropriate degree of substitution (1.5 to 3.0 ds) imparts thermoplasticity. Unmodified starch shows no thermal transitions except the onset of thermal degradation at around 260 °C. Starch acetate of ds 1.5 shows a sharp glass transition at 155 °C and starch propionate of same ds had a T_g of 128 °C. Plasticizers like glycerol triacetate and diethyl succinate are completely miscible with starch esters and can be used to improve processability. Water resistance of the starch esters is greatly improved over the unmodified starch.

EverCorn Inc., is commercializing biodegradable plastics based on starch esters and blends of starch esters with aliphatic polyesters. Appropriately formulated starch esters with plasticizers and other additives provide resin compositions that can be used to make injection molded products and for direct lamination onto Kraft paper. Starch acetates up to ds=2.5 undergo complete and rapid biodegradation. In the case of starch triacetates, 70% of the carbon is converted to CO₂ at 58°C in 45 days.

BLENDS, ALLOYS & GRAFT COPOLYMERS OF STARCH AND ALIPHATIC POLYESTERS

Starch-polyester blends are being evaluated for commercial applications. Starch can be incorporated in several ways:

- as a filled composite
- graft copolymerization
- plasticized starch phase in which the granular structure of starch has been disrupted.

In all these cases, the starch can either be in its native form or be physically or chemically modified.

Starch-Poly(ϵ -caprolactone) (PCL) alloy. This technology involves reactive extrusion processing of plasticized starch with modified PCL in a twin screw co-rotating extruder with modified screw elements. By controlling the rheology in the extruder, one can obtain a morphology in which the plastic starch is dispersed in a continuous PCL matrix phase. Good adhesion and compatibilization is promoted between the plastic-starch phase and the modified PCL phase to obtain enhanced mechanical properties.

Two other companies, Novamont, and Milleta (Biotech Division), are manufacturing and selling starch-PCL blends for film applications (compost bags, trash bags). Starch is plasticized using water or hydroxy solvents and blended with TONE 787 polymer from Union Carbide.

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Invited lecture

**NEW DERIVATIVES OF POLYSACCHARIDES
WITH THERMOPLASTIC CHARACTER**

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A novel process has been used to solubilise starch and some other polysaccharides. This allows the polymers to be derivatised uniformly along their length. By grafting side-chains onto these accessible polymers it is then possible to convert them into thermoplastics which have melting points in the temperature range 60–160°C which is of interest to industry. This paper reviews work exploring synthesis variables, and reports progress made in scaling up the new process and in investigating end uses for the new thermoplastics.

Invited lecture

**PULTRUDED JUTE FIBRE-BASED COMPOSITES
FOR BUILDING AND CONSTRUCTION**

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TIPCO Industries Ltd., the pioneers of Thermosetting Resins and Molding Materials in India, have developed technology for manufacture of products based on Natural Fiber Pultruded Composites. At its modern plant and R&D centre in Valsad, Tipco has developed specialty thermosetting resins, fiber treatments, special die designs, pultrusion process design for manufacture of multi-functional profiles of natural jute fiber composites for diversified applications in the building and construction industry. The technology edge, coupled with new, innovative product concepts, in the form of smart design Doors, Windows, Frames for door and windows, Office Partition Systems, Ceiling Systems, is geared towards replacement of wood to save the ecological balance. Tipwood® profiles made out of jute and synthetic thermosetting resins, look and feel like rich wood products, with mechanical, chemical properties and performance, superior to wood. The versatile Tipwood® Building Systems are tailor-made to suit special needs of builders, architects, building contractors, consultants, carpenters in private building projects, government housing schemes, municipal corporations, offices, homes, and factories. Tipco's future product developments include Roofing Systems, Pre-fabricated Housing Systems and Knock-down Furniture. One of India's leading plastics raw materials supplier, Tipco aims to provide technology turn-key projects, technical collaborations or franchises for Tipwood® Products, based on jute and other natural fibers, all around the world.

Invited lecture

PROPERTIES AND APPLICATIONS OF JUTE BASED COMPOSITES

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JUTE FIBRE

Jute is a natural fibre with a modulus and strength of 10 - 78 GPa and 600 - 900 MPa respectively and a specific gravity of 1.2. Around 3,000,000 tonnes are grown per annum in the hot wet climate of SE Asia. The sliver, produced after retting, is spun into twine and woven to give a fabric or cloth, with a weight per square metre of ~200 - 700 g. This was traditionally used to produce sacks and linoleum and for carpet backing. Up to 6% of a mineral based, batching oil is added to aid processing. The oil is responsible for giving jute products their characteristic odour. Today its presence is a disadvantage if jute sacks, for instance, are being used to package foodstuffs. The fibre begins to char at ~ 200°C and will eventually degrade in the presence of moisture and/or UV radiation. The properties quoted, which were determined from scaling up measurements on well made, aligned, composites, are variable because as a natural material performance depends on the exact growing area, the prevailing weather conditions, when the crop was harvested etc. The price of jute sliver and cloth in UK is variable. Sliver costs from £200-300 per tonne and cloth £400 -1000 per tonne depending on quality and availability.

COMPETITION

Jute products have been almost totally displaced in UK and Europe by those based primarily on polypropylene. This polymer, costing ~£700 - 1200 per tonne, has consistent properties, depending on grade, adequate for sacking, carpet backing etc., is odour free, does not contain additives which could contaminate foodstuffs and is impervious to moisture, dust and insects. In addition its supply is assured and the cost structure more stable than that of jute. The disadvantage (or advantage depending on how one looks at it) is that polypropylene is not biodegradable.

THE CHALLENGE

Jute growing and processing provides a livelihood for approximately 40,000,000 people in SE Asia (mainly in Bangladesh and India) and the loss of markets not only in Europe but, to some extent, indigenously poses a serious social / economic problem to, sometimes, fragile economies. Attempts have been made for five decades or more to find alternative uses for jute or use jute as a substitute material in times of crisis. The obvious approach has been to make jute composites using natural, inorganic, organic and polymer based binders. Beginning in 1995 AEA Technology plc headed up a three-year programme to do this in a

systematic way. The partners were ATO-DLO, The Netherlands and The Indian Institute of Packaging, Bombay, India. Technical monitoring was provided by The International Jute Organisation, Dhaka, Bangladesh and funding by The Common Fund for Commodities, The Netherlands. The programme studied the production and properties of jute sliver, felt and cloth composites, jute filled moulding compounds and uses of these products in rigid and flexible packaging and structural components. The programme was an interactive, international, one and the results quoted here are from all the partners.

JUTE COMPOSITES

Jute laminates were produced from up to 60% by volume of jute cloth, sliver, aligned unidirectionally or orthogonally and a specially produced felt with a fibre length of ~10 mm. Since it was concluded that washing the fibre to remove batching oil did not improve the properties this step was omitted as a cost saving measure. The fibre reinforcement was combined with epoxy, polyester or phenol formaldehyde thermosetting resin, sheet and/or powdered polyethylene or sheet polypropylene, inorganic binders such as silicates and organic materials including soy products, casein, cellulose diacetate, starches and ordinary flour. These ranged in price from ~£200 per tonne to over £5000 per tonne. In many cases the fibre was saturated with the liquid binder, pressed at ~1 MPa and heated for up to one hour at a temperature of up to 120°C to make a laminate ~ 70 x 70 cm square and 1 to 5 mm in thickness. Specific gravity ranged from 0.5, for very voidy, poorly compressed, material to virtually the theoretical upper limit of 1.2. The flexural strength was in the range 30 - 100 MPa and the modulus in the range 3 - 15 GPa depending on the fibre loading and orientation and quality of the moulding. Thermoplastic laminates were made by interleaving the reinforcement with 10 - 100 µm sheets of polymer and, in the case of polyethylene, the additional use of powdered polymer. Pressing was as for the thermosetting matrix but the temperature was increased to 160 - 200°C though the pressing time was only 30 seconds to several minutes. The temperature sometimes caused the jute to char and degraded the polymer. Nevertheless the improved impregnation and hence mechanical properties more than compensated for this. Attempts were made to improve the bonding by using plasma treated polyethylene and maleic anhydride modified polypropylene. The mechanical properties of thermoplastic composites were similar, or slightly lower, to those reported for thermosets, though the toughness, whether Charpy impact or tearing, was much better. On grounds of cost and material availability work was concentrated on jute sliver or cloth with a phenol formaldehyde resin or polyethylene sheet matrix. Apart from the specific gravities, which were approximately increased by 50%, the mechanical properties of the various systems were comparable with those of wood products, see Figure 1.

Much of the ATO-DLO programme concentrated on producing injection moulding compounds based on and either polyethylene or polypropylene with a maleic anhydride compatibiliser, reinforced with up to 50% of ultimate cells of jute. These materials were moulded into rods, bars and sheets and had moduli and strengths in the range 1 - 3 GPa and 30 - 80 MPa respectively.

USES OF MATERIALS

The laminates were initially used to produce tea chests either with the traditional wooden battens or moulded jute side brackets adhesively bonded or hot welded into position. The stiffness, and hence dimensional stability, of a jute composite chest with a weight

comparable to that of a conventional wooden one, proved to be inadequate. To increase the thickness of the jute laminate would have not been cost or weight competitive, and this, combined with rapid changes that were taking place in the tea importing and handling industry in UK, caused us to cease work on this application. Jute fabric laminated with polyethylene / Al / PET was, however, successfully used to fabricate flexible packaging for the transportation of tea. The PE bonds well to the jute when heat pressed; the thin evaporated aluminium layer with the thermally stable PET give a weather resistant hermetic outer layer. This type of packaging is cost competitive with the aluminium lined plied craft paper sacks which have replaced many of the more traditional plywood chests for the bulk transportation of tea.

Contacts with a resin transfer moulding company, already making composite products for the automotive industry, showed that combinations of jute felt, fabric and knitted material could be successfully injected with a polyester resin without any special preparation of the charge, other than cutting to shape. A specimen parcel shelf is shown in Figure 2. The ~2 x 1 meter moulded shelf had very similar mechanical properties to a GRP one. The company sees much potential in the product and would consider, with proper backing, setting up a plant in SE Asia.

A jute tape was successfully pultruded using a phenolic matrix to make a 90 degree bracket. Combinations of jute fabric and sliver can be used as the basis of pultruded products to lower the cost of fully glass reinforced pultrusions.

The chopped jute filled moulding compound can be injection processed to make crates and other reusable packaging materials for the fruit and vegetable market in Europe. This approach gives the potential for reducing the cost of the moulding compound whilst at the same time increasing the strength and modulus.

COSTS

The estimated materials and finished product costs for sliver/ thermoset are 0.53 - 0.76 £ per kg and 1.0 - 1.5 £ per kg respectively. Similar figures for jute fabric/polyethylene are 1.0 £ per kg and 2.0 £ per kg respectively. Both these materials can be used to make rigid containers. For a flexible fabric/polyethylene material, suitable for making sacks, the figures are 0.45 - 1.0 £ per kg and 0.7 - 1.25 £ per kg respectively. Large scale production, with properly sourced supplies of fibre and polymer, would possibly result in a reduction in these figures. In all of these uses it should be possible to produce components which are cheaper than, and with as good properties as, ones made from polymer or GRP, provided the cost of the jute is stable and the quality and quantity assured.

CONCLUSION

The project has demonstrated that it is possible to make rigid jute composites with properties comparable to those of wood, polymer and GRP products. Because of the competitive nature of the marketplace and the need to avoid the added cost of exporting jute it is recommended that this development takes place in SE Asia, where jute is produced, labour costs are lower and the availability of wood products, at a competitive price, is less assured.

Invited lecture

SURFACE ENGINEERED CELLULOSE FIBERS WITH HIGH PERFORMANCE

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There is increasing interest in preparing new materials based on renewable resources. In this laboratory, we have prepared a new generation of stimuli-responsive fiber hydrogel hybrid materials based on cellulose. pH-sensitive cellulose fiber-supported hydrogels were prepared by ozone-induced graft polymerization of acrylic acid using cotton linters and wood pulp fiber substrates. Grafted polyacrylic acid was present not only at the surface but was also homogeneously distributed within the pores of the fibers. A fiber-supported hydrogel, which exhibited reversible swelling and deswelling, was prepared by an addition of a bifunctional monomer to the monomer solution used for grafting. Such muscle-like expansion and contraction was also stimulated by pH changes in the environment.

Recently we have evaluated hemicelluloses, particularly xylans from hardwood, as raw materials for making hydrogels. Although hemicelluloses are believed to play an important role in the formation of wood hierarchy, these polymers have not yet been utilized as building blocks for new materials. In this research, the crystallization of hemicellulose (xylan) from hardwood has been studied as a function of molecular weight and chemical composition. Cellulose fiber surfaces were used for the nucleation of xylan crystallization from solutions, and growth was controlled by varying the chemical potential. The crystallization process was followed with Wide-Angle X-ray Scattering (WAXS) and AFM techniques. The aim of this research is to prepare novel materials inspired by the hierarchical structure of wood.

Invited lecture

JUTE FIBER FOR REINFORCED COMPOSITES AND ITS PROSPECTS

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Jute, the fiber of commerce in India, is an annual plant of tropical countries obtained from the stem of cultivated varieties of the two species *Corchorus Capillaries* L.(white jute) and *C. Olitorius* L. (tosa jute). The total area under cultivation is approximately 0.9 million hectare and yield is 2 MT/hectare. Jute ranks next to cotton as the most important natural fiber in the world. Jute, in India, provides livelihood to around 4 million farmers and 362 thousand workers.

Jute fiber contains (12-14%) lignin, (21-24%) hemicellulose and cellulose (58-63%) along with trace ingredients like nitrogenous matter, fats, waxes and ash. It is a harsh fiber due to presence of substantial amount of lignin and low wax content. Moreover, the presence of cellulose backbone in a lignin matrix makes it the stiffest among natural fibers and this is the basic reason for its technical non-viability as a textile fiber from spinning point of view. However, these limitations give an important design criteria for the development of fiber reinforced composites. The tensile strength, tensile modulus and elongation at break are 442 MPa, 56 GPa and 1.3% respectively. Due its lower specific gravity, its specific properties are favorable to the material scientist and comparable to glass. The specific tensile strength is 303 MPa, about 22.5% of glass and specific tensile modulus is 38.4 GPa which is about 35% more than glass. The choice of jute as a reinforcing fiber is mainly due to its good specific mechanical properties, low cost and good availability. The long fiber and its flexibility also confers very good impact strength. Its less abrasive nature augment the machinery life.

In spite of all these advantages, the fiber bears the drawback of non-resistance to high temperature, susceptible to moisture absorption and mildew attack. For this, chemical modification is required to develop performance driven composites.

The use of straw in the mud huts from ancient times probably the pre-cursor of the modern man made composites. The use of bio-based composites has rapidly expanded in recent years and there is tremendous potential for future growth in this area. The reason for this is mainly two fold. One is to resist deforestation and the other, there is demand of new materials due to growth of world population. The uses range from automotive interior components to geotextiles. A broad range of agro-based fibers is utilized as the main structural components or as fillers / reinforcing agents in these composite materials.

The most commonly known natural composite is wood. Continuous use of wood for different applications such as furniture, packaging, pulps, fuel, and construction materials has resulted in a drastic deforestation. There is a great need to develop natural composites to substitute for wood.

Between 1952 and 1988, in 36 years, the forest cover in India has gone from 22 to 12% of the total area i.e. @ 0.4% per annum. The Food and Agricultural Organization of the United Nations (FAO) has estimated that India lost 3.4 million hectares of tree cover between 1951 and 1972, which means 1,55,000 hectares are lost per annum. The depletion of the forest caused environmental pollution and forced the Supreme Court of India to ban forest cutting. So there is a great demand for wood substitutes but there is also a resistance to accept jute as a viable substitute.

Glass fiber, asbestos and cotton are the most frequently used reinforcing fiber by the composite industries. The high cost and good mechanical properties of glass fiber composites are not often justified as substitutes for wood. The use of asbestos has been restricted due to its carcinogenic effect and cotton is also a costly proposition for its use as a reinforcing fiber for the development of wood substitute. Considering these facts jute fiber has a future as a low cost reinforcing fiber for the development of jute composites.

Commercial production of jute board from jute fabric, jute non-woven using water soluble thermosetting resins has already been started by two companies in India. More companies are developing composites for Indian Railways for coach building purposes and other domestic needs for the replacement of wood and plywood. The method of production includes the simple route of impregnation, drying and pressing in the multi-daylight hydraulic press following the compression molding technology under heat and pressure.

For automotive interior applications, jute non-woven polyester systems are already commercial. IJIRA is working on jute polypropylene calandered sheet similar to wood fiber polypropylene available in the advanced countries. Though jute fiber is very costly as compared to wood fiber, the use of waste jute from the jute mill may be considered for the cost reduction purposes. The major drawback for the implementation of this technology is the very high cost of imported machinery.

The traditional pultrusion process is simple continuous fiber reinforcement in which fiber is pulled through a bath of thermosetting resin and then through a hot die where consolidation and curing occur. After curing the composite profile is cut to the required length. Use of jute fabric, yarn, non-woven with phenolic/polyester matrix were successfully done for the production of different profiles including door frame and U-channels.

Resin transfer molding is very popular using glass substrates. For applications, where very high cost and strength is not justified, jute can be used either in the core or the total glass may be replaced. Due to very low bulk density of jute as compared to glass little modification is required in mold making. This jute-RTM technology has a bright future for items like door, automotive component, instrument panel, truck hood, and bonnets.

Invited lecture

NOVEL ADHESIVE SYSTEMS BASED ON PLANT DERIVATIVES

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The wood based panels industry relies almost entirely on formaldehyde-based or polyurethane-based adhesives. In different parts of the world, the consumer associates the former with problems of formaldehyde emission, and the latter with greater risk in the workplace and greater toxicity of smoke in fire. Whether or not these consumer perceptions are valid, there is growing interest in so-called bio-based adhesive systems. In the last few years, new systems based on enzyme activation or on derivatised carbohydrates, phenolics or tri-glycerides have been under development in parallel in a number of research centres. This paper reviews the state of the art in the context of the three issues critical to the panel manufacturer: cost, curing rate, and performance.

Invited lecture

**COMPOSITES MADE FROM LIGNOCELLULOSIC
MATERIALS AND THERMOSET POLYMERS**

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Composites made from an unsaturated polyester/styrene thermoset matrix and (maleic anhydride) esterified woodflour have been prepared and tested. Different degrees of esterification of the wood particles were obtained by using different times of reaction, which lead to materials with varied final properties. Water absorption, flexural compression and dynamico-mechanical tests were performed on the composites to find out an optimum level of chemical modification of the woodflour. Moreover, the relationship between the filler content and the composite final properties was also studied for the selected filler treatment. An important increment in particle dispersion was obtained by modifying the woodflour with maleic anhydride.

INTRODUCTION

The use of vegetable fibers and/or particles as reinforcement/ fillers for polymeric matrices has been enjoying a continuous growing interest in the past decade from the academic and applied points of view. Applications go beyond the widely used particle board and efforts are being made to produce insumes for the construction, packaging and automotive industries among others.

Unfortunately, the frequent incompatibility between lignocellulosic materials and many polymeric matrices affects the degree of dispersion of the fibers in the matrix and the overall homogeneity of the structural piece. However, the addition of a compatibilizing and/or coupling agents to the filler or to the compounded material usually results in improved final properties^{1,2}.

In this work, the final properties of composites made from a thermoset matrix and chemically treated woodflours were measured and related to the degree of modification and the filler content.

EXPERIMENTAL

The matrix was an unsaturated polyester (RQ 426, Perlinac S. A., Argentina) crosslinked with styrene in a 60:40 weight proportion with no additives and using benzoyl peroxide as initiator (1.5% wt. with respect to the reaction mixture). Woodflour from *Eucalyptus Saligna* ($\rho = 830 \text{ Kg/m}^3$) was selected for this work because of its availability and widespread use in Argentina. Particles passing through a sieve-mesh 250 (Tyler series) were used in this study (av. size $57 \mu\text{m}$).

Woodflour was dried, pretreated with an alkaline solution and washed before the esterification step. The particles were immersed in a 0.6 N solution of MAN in xylene and then heated at reflux temperature (140°C) during 4, 7 or 24 hours (depending on the desired reaction level). The wood particles were separated from the solution and washed with distilled water to eliminate the unreacted anhydride. Finally, they were dried at 70°C under vacuum.

Filler and resin were compounded in an intensive mixer. The paste was molded and cured at 80°C during 1.5 h, under a pressure of 3.8 MPa. Then, it was postcured for 2 hours at 150°C.

RESULTS AND DISCUSSION

Table I shows the % increment in weight of the woodflour after the esterification and the equilibrium moisture content measured at room temperature (20°C) and 90 % relative humidity.

Table I: Level of esterification (as gMAN/100g woodflour) and equilibrium moisture content (EMC %) of differently treated woodflours and compression properties of composites made with 40% of filler .

Woodflour Treatment	Esterification level (MAN wt. %)	EMC (wt.%) at 90 RH	σ_y (MPa)	Toughness (MPa)
none		14.72	140.9 \pm 2.6	10.5 \pm 3.8
NaOH	-----	29.89	130.1 \pm 11.8	11.8 \pm 1.13
MAN - 4 hs	10.96	12.91	138.2 \pm 4.8	26.4 \pm 6.5
MAN - 7 hs	30.58	10.38	136.8 \pm 0.8	30.7 \pm 7.4
MAN - 24 hs	58.30	12.22	138.6 \pm 6.3	28.5 \pm 13.5

The alkaline treatment increases the hygroscopicity of the woodflour, which is reduced by further esterification. However, the difference in equilibrium moisture content of the particles at different esterification levels is negligible.

Compressive tests of the materials showed differences between treated woodflours. Values of yield stress and toughness (as area under the σ - ϵ curve)³ are also reported in Table I. These results indicate an interesting improvement in properties of the composites if the woodflour is esterified, but the differences with levels of treatment are negligible. Thus, the 4 hs esterification treatment was selected and the effect of varying the filler content was further investigated.

The chemical modification allowed to greatly improve the dispersion of the particles in the mixture: only 40% (wt.) of the alkaline treated woodflour could be loaded and up to 75% of the MAN treated particles was compounded. The mechanical properties of the material go through a maximum at about 60% of filler. At this composition a yield stress of 172.8 MPa is reached with a modulus of 3.9 GPa. However, the toughness drops with the filler content down to 14 MPa.

Acknowledgments

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Invited lecture

PROCESSING TECHNOLOGIES FOR AGROFIBRE REINFORCED THERMOSET COMPOSITES

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INTRODUCTION

Over the last decades several production technologies have been developed for processing fibre reinforced thermoset resins. These production technologies are restricted to smaller scale utilisation, in contrast to fibre reinforced thermoplastic composite materials. However, the superior properties of the materials make thermosets indispensable for a number of end-uses. With the recently widespread targets of sustainability of production and consumption in mind, lignocellulosic fibres have been identified as a potential substitute for commonly applied glass fibre reinforcement. However, it should be noticed that agrofibre is composed of fibres, actually composites in itself, which makes it impossible to simply substitute glass fibres by agrofibre. ATO-DLO has recently studied several ways to produce agrofibre reinforced thermoset composites, considering the specific structure of agrofibre.

FIBRE-MATRIX INTERACTION

The specific properties of a composite material is the result of the physical properties of its constituents, generally the matrix and the reinforcing fibres, but also of the specific interaction of both. If the fibre-matrix interaction is poor, it is impossible to produce a satisfying reinforced material. The fibre-matrix interaction might be poor due to differences in surface tension, which is, for example, the case for flax fibres and an epoxy or polyester matrix. Much research has been carried out on the modification of the agrofibre-matrix interface, trying to bridge the two constituents by grafting or derivatisation of the fibre (surface) or adaptation of the resin formulation. Some of those methods are improving the compatibility of the fibre and matrix, but many methods seriously affect the fibre mechanical properties. Therefore it is essential to understand the specific surface properties of the components in the compound and the balance between adhesive and repulsive forces, which results in the product properties.

THERMOSET COMPOSITES BASED ON AGROFIBRE YARN AND FABRIC

Lignocellulosic fibres have a number of advantages over glass fibres, such as renewability, incineration without large production of ash, low density. In contrast to glass fibres, however, the natural cellulosic fibres are not obtained as continuous filaments, but are

limited to the maximum dimensions of the plant fibre cells. These discontinuous fibres can be spun into an infinite yarn, however, during the traditional processes to produce yarns and fabrics - from fibre extraction, to spinning and weaving - a large number of the intrinsic fibre properties are lost. Therefore the composites manufactured by filament winding using natural fibre yarns or by resin transfer moulding using a stacking of fabric layers show disappointing results. This is partly due to so called 'kink-bands', which are caused by mechanical treatments, like scutching, hackling, carding and spinning and which significantly reduce the fibre strength. Furthermore, the fibre orientation in those systems is not really unidirectional or (0,90) degree because of the twisted and entwined nature of the yarns, so the net contribution of the fibres to the composite strength in the main directions will be lower than may be expected on basis of full exploitation of the intrinsically present fibre properties. Other aspects of fibre-fibre interaction play also an important role. To exploit the maximum of the mechanical properties of the agrofibre in a composite material, its intrinsic nature has to be considered.

SHEET MOULDING COMPOUND TECHNOLOGY

Sheet Moulding Compounds (SMC), random glass fibre oriented polyester composites, are manufactured for automotive applications and for consumer goods. For the production of SMC materials continuous glass roving, which is cut to lengths of 25-50 mm, is used. Instead of glass roving, e.g. flax sliver can be used. Differences in processing for glass and flax fibres are mainly based on the difference in density. Because of the low density, agrofibre have a different sprinkling and spreading behaviour than glass fibres. Furthermore, when using the same weight fraction of fibres in the composite, a higher volume of flax fibres has to be impregnated compared to glass fibres, so special attention has to be considered. Apart from these processing items, the form in which the fibres are packed in the composites has an influence on the composite mechanical properties.

BULK- AND EXTRUSION MOULDING COMPOUND

Short glass fibre reinforced thermoset composites are manufactured via the Bulk Moulding Compound (BMC) technique: glass fibres are mixed with polyester in a batch kneeder. Subsequently the material is given its final form via an injection moulding or compression moulding technique. The glass fibres can be substituted by agrofibre without large adaptations to the process. A number of specific differences in interactions during the compounding and curing processes of cellulose fibre and thermoset matrices are relevant for the final result. The rheological properties of the resin and the wettability of the fibre by the resin directly affect the penetration of the resin in the fibre and the gripping of the fibre in the matrix and therefore control the adhesion between fibre and matrix. However, most important is the control of the curing process, which can be largely controlled by avoiding the building up of pressure during the blending of fibre and resin. The kinetics of the curing process can be controlled by regulation of the temperature and pressure or addition of inhibitors and initiators for the polymerization process. Depending on the scale of production, the pre-mixing of the fibres and the polyester can be performed using an extruder instead of a batch kneeder.

In conclusion can be said that the use of agrofibre in thermoset composite materials, as described above, needs special attention with respect to the specific fibre properties and the form in which the fibres are blended into the matrix, as well as adaptation of resin formulations.

Invited lecture

**INFLUENCE OF ARCHITECTURE ON MACROSCOPIC
PROPERTIES OF WOOD FIBRE MATS**

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Wood fibre composite materials, such as paper, insulation boards, MDF, or wood polymers composites, exhibit a complex structure, depending on the way they are processed, and the compatibility with the matrix when there is a matrix. This structure is expected to affect the macroscopic behaviour of these materials, and especially the way damage proceeds in the heterogeneous field. With the huge development of finite element calculation capabilities it is now possible to use information on the architectural properties of heterogeneous materials in predictive models of their macroscopic behaviour. In this paper we will especially investigate damage processes in consolidated fibre mats, that may or may not include a thermoplastic resin.

Invited lecture

WEATHERING PERFORMANCE OF PLANT-FIBER/ THERMOPLASTIC COMPOSITES

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Natural fiber/thermoplastic composites were made using aspen fiber and polypropylene. Several different levels of fiber were used with and without the addition of a compatibilizer. For composites containing 30% aspen fiber and either 70% polypropylene or 68% polypropylene and 2% maleic anhydride grafted polypropylene, cyclic humidity testing between 30 % RH and 90% RH showed that there was a small but steady increase in moisture sorption with each humidity cycle. Weathering of both composites under accelerated weathering conditions (water sprayed for 18 minutes followed by 102 minutes without water spray of UV radiation produced by a 6500-watt xenon arc light source) was restricted to the outer 0.5 mm of the surface. Weathering gave rise to the development of a white chalky surface layer after about 600 hours of weathering and, after 1400 hours there was a loss in surface smoothness. After 2000 hours of accelerated weathering, the specimens without compatibilizer lost 3.9% weight while the specimens with compatibilizer lost 2.9% weight.

It is well known that polypropylene is not stable to UV radiation. With a large number of tertiary carbon sites, polypropylene is very sensitive to free radical formation and decomposition by chain scission resulting in the formation of lower molecular weight polymers on the surface. Agro-based fibers also undergo UV degradation through free radical reactions with the decomposition of the lignin polymer in the cell wall.

Swelling of the composites by moisture results in an increase in UV degradation as swelling develops new surfaces exposing more polymers to degradation.

Composites were also made using 30%, 40%, 50%, and 60% aspen fiber in combination with polypropylene alone or with 2% maleic anhydride grafted polypropylene. These composites were exposed to both cyclic liquid water and humidity tests and evaluated in an accelerated weathering test for 2000 hours. Results of these tests will be presented

Invited lecture

**NATURAL FIBRE COMPOSITES MANUFACTURED
WITH THE RESIN TRANSFER MOULDING
PROCESSING TECHNIQUE**

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In this work the use of natural fibres as reinforcements was studied with the resin transfer moulding (RTM) processing technique. Flax fibres, retted in different ways, were used as reinforcement in an epoxy (E) resin. The mechanical properties of the composites were compared to conventional RTM glass fiber composites and to the pure epoxy resin.

The results from the mechanical testing showed that the enzyme retted flax fiber/epoxy composite (50/50) has a stiffness of about 40 GPa compared to the stiffness of glass fiber composites 30 GPa (with similar fiber content) and the pure epoxy of 3.2 GPa. The same flax/epoxy composite has a tensile strength of 280 MPa compared to glass fibre composites 820 MPa and 80 MPa of the epoxy. These preliminary strength properties shows that the natural fibre composite do not reach at the level of glass fibre composites which is not even expected due the lower strength values from the literature. But it is interesting to notice that the weight related strength and stiffness of the enzyme retted flax fibre composites can compete with the glass fibre composites. The specific strength of the flax/epoxy composite was 210 MPa/gcm^{-3} compared to the 470 MPa/gcm^{-3} of the glass/epoxy composite. The specific modulus was 29 GPa/gcm^{-3} , which is superiour, compared to the glass/epoxy composites 18 GPa/gcm^{-3} .

The study of the composite microstructure showed good interfacial adhesion between the flax fibres and the epoxy matrix. Biotechnical processing of natural fibers showed to result in good fiber quality and high mechanical properties if compared to conventional dew retted natural fibers. RTM showed to be a suitable processing technique for natural fiber composites when high quality laminates are preferred.

Invited lecture

**WOOD POLYMER COMPOSITES MADE
BY THE POLYMERIZATION OF CHEMICALS
INSIDE SOLID WOOD**

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Wood polymer composites (WPC), in the context of this paper, are composites made from solid wood and monomers that are polymerized inside the wood. Improvement of physical properties of wood is usually the reason for making WPC. This paper reviews how they are made, the chemicals used, and the physical properties of WPC. Some actual and potential applications of WPC are discussed.

Methyl methacrylate (MMA) appears in the literature more frequently than any other monomer used to make WPC. It is among the least expensive and more readily available monomers for this purpose. MMA is used alone or in combination with other monomers. Styrene is a monomer also used frequently to make WPC, often with unsaturated polyesters. Styrene is readily available, relatively inexpensive, and gives WPC many of the desired properties. Surface hardness, water repellency, dimensional stability, abrasion resistance, and fire resistance are properties that are important to those making WPC. Other properties that may be important are improved toughness, strength, decay resistance, and resistance to weathering. Some properties are obtained easily but others such as dimensional stability and fire resistance are more difficult to obtain.

The production of WPC hardwood flooring is a large use for WPC. Other uses or potential uses are the manufacture of furniture, sports equipment, and parts for musical instruments. There may also be future industrial applications and uses as construction materials.

Invited lecture

IMPROVEMENTS IN DECAY RESISTANCE BASED ON MOISTURE EXCLUSION

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Moisture content has an effect on the biological decay of wood. The literature states that serious decay occurs when the moisture content of wood is above the fiber saturation point (FSP), which is the measurement of the moisture content of wood when the cell walls are saturated and the cell cavities free from water (average 30%). Chemically we can modify wood hydroxyls by various treatments i.e. acetylation, isocyanates, and epoxides, and thus lower the FSP. If we alter the hydrolytic bond, wood cannot get wet because it cannot hydrogen bond, although “free” water can still be present in the voids or lumens. So is biological protection as simple as modifying the hydroxyl groups? Investigations are underway to chemically modify wood and fiber samples and evaluate them biologically by the soil block test, as well as by the FSP and the equilibrium moisture content (EMC). EMC is the moisture content of wood at any given relative humidity and temperature. Potential correlation between moisture exclusion and biological protection will be discussed.

Invited lecture

**THEORETICAL LIMITS AND MEANS OF PROPERTY
ENHANCEMENT IN NATURAL FIBER COMPOSITES**

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Natural fiber composites are gaining acceptance for use in a myriad of applications, from automotive parts to household items. However, the strengths of the composites reported in literature are far below what is theoretically possible. Several factors determine the efficiency of the composites, and some important ones are fiber length or fiber aspect ratio, stress-transfer efficiency and fiber orientation. Unless one understands the role of each of the above factors, it is difficult to design composites with the properties close or equal to that which are theoretically possible.

This paper will cover some basics of composites, and will deal with all the important factors that govern composite behavior. The effect of changing some of the factors and the subsequent effect on composite properties will be discussed. Recent experimental data will be presented to show how these factors effect properties. Experimental techniques such as fiber modification and additives that result in property enhancement will be discussed.

THE EFFECT OF FROST ON FIBRE PLANTS AND THEIR PROCESSING

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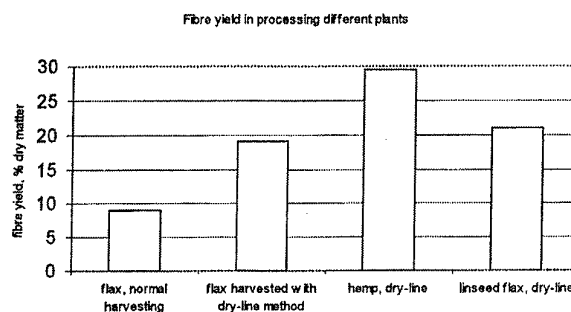
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Harvesting flax and hemp fibres in the autumn often meets with special problems in the Nordic climates. These are mainly due to the short growing period and the cold and rainy periods in autumn. The risk of formation of mold spores inside the harvested fibre plant bales is obvious (1). Even though the bales are dried in a bale driers there is enough time for the molds to destroy the quality of the raw material. This is caused by both the slow drying process and the high microbiological activity in the moist material (3). This is the reason why the new Dry-line-method (2) is under research. Briefly the dry-line-method is: harvesting the seeds in the autumn which is the driest time for the plant; harvesting the straw in the spring which is the driest time of the year getting benefit from the good friction and processing properties of dry plant material.

The frost has a special effect in Northern countries. In the springtime, the temperature is changing daily above and below the freezing point. This leads to freezing water in the plant which is different for different parts of the plant cell structures. When this takes place repeatedly several times the movement also loosens the bast fibre from the stem. In this research the temperature was measured among the plants. Also, the yield of fibre was measured after different processing of raw material (Table 1). Energy demands of the processing of the plant material was reduced drastic compared to unretted or dew retted material. Also, the yield of the processed fibre from the plant raw material was higher compared to material which was not frozen. The latter is due to both the higher loss of shives before and during the processing and the better separation of fibre and shives during and after the processing.

**Table 1. The fibre yields
of different plants**



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DIFFERENT INFLUENCES OF COTTON AND POLYPROPYLENE UNDERWEAR ON THERMOREGULATORY RESPONSES AND CLOTHING MICROCLIMATE IN THE COLD

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The present experiment aimed at knowing whether cotton and polypropylene underwear may influence differently human thermoregulatory responses and clothing microclimate in the cold, in the participant during 30 min heavy exercise and 60 min recovery. An ambient temperature was kept at 0° C. The participant sweated considerably during the exercise. The participant wore either cotton (one/two layers/ and polypropylene/ one/two layers) underwear and heavy ski suit including polyester padding. The main results are summarized as follows:

1. Core temperature fell down more greatly during the recovery in polypropylene underwear.
2. Metabolic heat production was significantly higher during the recovery in polypropylene underwear, suggesting that dry heat loss occurred more greatly from human body through clothing to surrounding air in polypropylene.
3. Clothing humidity was higher within ski suit during the exercising and recovery period in polypropylene.
4. Temperature difference between clothing microclimate in the innermost and that within ski suit was significantly lower in polypropylene, indicating that the heat flow from skin area to the ski suit was great in polypropylene.

We discuss these findings in terms of human physiology and clothing sciences.

STUDY ON THE PERSULPHATE BEHAVIOUR OF BUTYL ACRYLATEGRAFT COPOLYMERIZATION ONTO MAIZE STARCH

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Graft copolymerization of butyl acrylate (Bu A) onto starch using potassium persulphate as free radical initiator was investigated. The study was included a comparison between applying the persulphate alone as free radical initiator and persulphate / thiosulphate as redox system initiator. Emphasis was placed on the promotion of graft copolymerization with a rational homopolymerization. This could be achieved through a thorough investigation onto the major factors affecting the polymerization reaction. State of starch (granules or highly swollen starch).; HSS, type and concentration of initiator, monomer concentration, time, temperature and material : liquor ratio were studied. The magnitude of the polymer yield including; the total conversion (TC), graft yield (GY) and homopolymer (H), have-been used to evaluate the polymerization reactions. On base of the mechanism of the grafting reaction is discussed.

MODIFICATION OF NATURAL POLYMERS PRESENT STATE AND FORECAST

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The requirement of new polymeric materials with special properties such as biodegradability, biocompatibility, bioactivity, thermal stability or environmental friendly behaviour is going to be based more and more on the naturally originated polymers. Several modifications of natural polymers such as cellulose, lignin, starch or chitin have produced the polymeric materials with improved or new properties.

A present state of the modification of natural polymers such as cellulose, lignin, starch and chitosan related to their processing to the valuable products applicable in chemical fibres, textiles, resins, agriculture or medicine is going to be presented basing mainly on the results of own research. A special emphasis on the modification of cellulose to produce the cellulosic fibres using environmentally friendly technologies will be carried out. A description of the present status on the modification of lignin and starch for their transformation to the high performance polymeric materials is planned. A special impact on the modification of chitosan, both by physical – chemical and chemical methods, to create the special chitosan – based materials useable in technics, agriculture or medicine will be discussed.

At the same time a forecast on the modifications of natural, renewable polymers will be prepared.

THE USE OF FROST PROCESSED REED CANARY GRASS FOR OIL SPILL ABSORPTION

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Reed Canary Grass (RCG) (*Phalaris arundinacea*) was used in a research project as a raw material for pulp and paper production (1). The yield of the harvested fiber in the spring, after plant growth was complete and when the moisture contents were very low was approximately 10-15% w.b. This harvesting method has been tested in the Department of Agricultural Engineering since 1991, first in the RCG harvesting and later also as "dry-line" method (2) in the harvesting of flax and hemp. In dry-line -method the seeds of fibre plants are harvested in the autumn but the straw is harvested in the spring when it is dry and well retted.

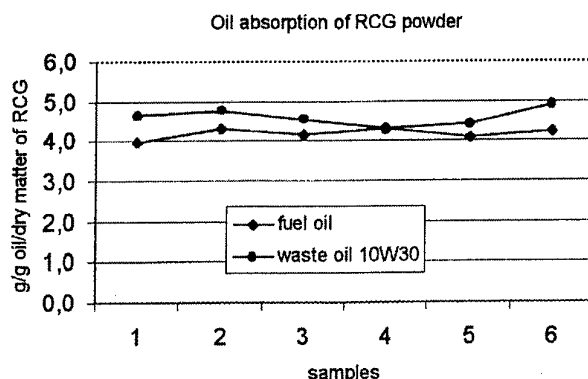
As a raw material for paper, RCG the high silicate content caused some problems because silicate was clogging some pulp mill pipelines. This problem was solved by separating the high silicate concentrate in a different fraction. This fraction proved to be a useful material in absorbing oil spills (3).

The plant material was milled with a hammer mill with 8 - 20 mm sieve. After that the powder was fractionated with a 1 mm sieve, the underflow of the powder was used in oil absorption. There are several reasons for the adsorption of hydrocarbons in RCG-powder. This problem is studied in a licenciate thesis of the author of this text. The main reasons for the oil adsorption phenomena seem to be:

- The adsorption and colloid action of the small particles in the powder and liquids
- The capillary absorption of oil in the perforated and empty ice-broken cells
- The effect of small diameter silicate particles in flocculation of oil droplets
- The effect of silicate compounds in bulk oil viscosity and flux in a RCG filter

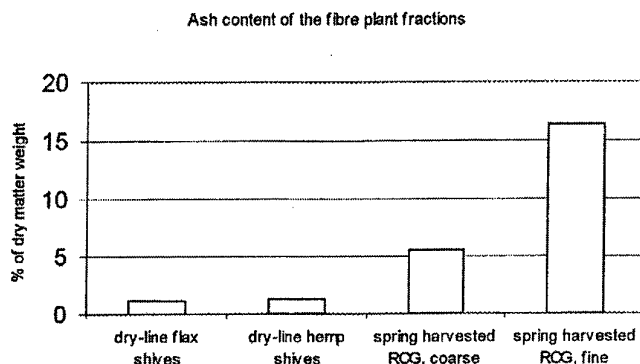
The oil absorption capacity on the RCG-powder was measured.

Table 1. The fuel oil and waste oil absorption of RCG powder.



The concentration of ash and silicate was measured in different fractions of a standard sieve (4).

Table 2. The ash concentration of spring harvested RCG, flax and hemp shives



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MELTING BEHAVIOR OF POLY(TETRAMETHYLENE SUCCINATE) AS STUDIED BY REAL-TIME X-RAY SCATTERING

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Time-resolved synchrotron X-ray techniques have proven very effective to elucidate rapid structural changes in polymers. For example, the crystallization and melting of polyethylene^{1,2}, its blend(LDPE/HDPE)^{3,4} and single crystals⁵ have been successfully studied by the small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) in real time.

Poly tetra methylene succinate (PTMS) has been known as a promising biodegradable synthetic polymer. Its thermal and physical properties are comparable with other common polymers of commercial products, so extensive studies have been carried out on homopolymer, blends, and copolymers with aromatic polyesters. Despite much demands from industrial fields, little work has been done on the processing of PTMS. And the preceding study on the crystallization and melting behaviour of polymers is inevitable to investigate polymer processing.

In the course of studying the melting behaviors of PTMS, we observed the multiple melting endotherms during the DSC heating scan. In one of the DSC curves we note three distinct melting endotherms; one small shoulder near 99 C and two relatively strong melting peaks at 108 and 112 C, respectively. It is apparent that the small low endotherm arises from the melting of less populated secondary lamella units of relatively thin lamella thickness. The other two middle and high endotherms, on the other hand, can be attributed to the melting of primary lamella units. However, the question remains whether the two endotherms are associated with the dual lamellar thickness or the melting recrystallization process.

In an attempt to elucidate the origin of the dual endotherms observed in the PTMS, we conducted the time resolved SAXS experiments utilizing the synchrotron radiation source at the Pohang Light Source in Korea. For the effective control of temperatures during the SAXS measurements a temperature jumping device, consisting of dual thermal blocks and a motor-controlled piston, was utilized. All the experimental conditions including the isothermal crystallization and heating rate were identical to those used in the DSC measurements except the cooling rate to the room temperature due to the limitation of apparatus. Each SAXS profile was collected for 10 sec. using an one-dimensional position sensitive diode array.

For the first time direct evidence confirming the melt-recrystallization phenomenon upon heating the semi-crystalline polymer was observed through the time resolved small and wide angle X-ray scattering. The fine structural changes observed by the time resolved SAXS using synchrotron radiation, during heating the PTMS crystallized isothermally at 95 C, revealed that the three melting endotherms on DSC scan represented multiple melting processes. The low temperature endotherm was due to the melting of less populated secondary lamella units and the middle and high endotherms were attributed to the melting of the primary lamellae and the melting of recrystallized lamellar units, respectively.

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STRUCTURE AND PROPERTIES OF COMPOSITES OF NATURAL FIBERS AND THERMOPLASTICS

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The study on composites of engineering polymers (EP) with natural components like wood fibre, flax, hemp, ramie etc. are recently intensively developed because of the ecology and interesting physical properties of such material [1,2]. One of the essential questions is adhesion between hydrophobic EP matrix and hydrophilic surface of the natural fibres (NF) in order to obtain composites with requested mechanical properties [3]. On the other hand, the NF component can act as a nucleant for thermoplastic polymer causing changes in morphology of matrix or even changes in arrangement of chains in crystal lattice what also strongly determine properties of final product.

In this work we will present results of our study on composites of isotactic polypropylene with flax and hemp fibres. We have used short (length 1-2 mm) as well as long flax and hemp fibres, which were unmodified and chemically modified. The composites with short fibres were prepared by extrusion and injection moulding process [4,5] and with longer fibres by press method. The morphology of the NF and structure of polypropylene matrix were examined by means of WAXS, optical microscopy AFM and DSC methods after processing. It was found that flax and hemp fibres induce hexagonal (β) arrangement of iPP chains which exist together with the monoclinic (α) form and amount of the β -phase depended on temperature and rate of cooling of injection mould [6]. These last observations in connection with literature data [7, 8] lead us to conclusion that one of the reasons of creation of the β -polymorph is difference in mobility of both components during solidification of polypropylene matrix in injection mould. In other words, the observed polymorphism can be considered as an effect of shear forces in the neighbourhood of NF surfaces. This hypothesis was confirmed by model investigations where the crude or chemically modified flax (FF) or hemp (HF) fibres were put in motion at various temperatures crystallisation of polypropylene. It was found that in iPP/NF system the hexagonal modification of iPP arises only when the fibres are put in a motion. The content of β phase significantly depends on temperature at which the fibres were moved. Unexpectedly, after chemical modification of NF the content of β phase lowered [9]. Therefore, the improvement of adhesion cannot be directly connected with nucleation ability of NF. Taking into account the results described by Wang et al. [10] we have supposed that topography of NF surface is responsible for specific interaction between NF and iPP matrix. It was analysed by SEM method. The others features noticed in investigated systems were transcrystallisation layers observed by OM and AFM methods.

ACKNOWLEDGEMENTS:

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PROPERTIES OF PVC-NATURAL POLYMER BLENDS

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The blends of recalcitrant to microbial attack thermoplastic polymers with natural polymers, which are susceptible to enzymatic degradation, have generated much interest recently. These materials, so called “partially biodecomposable” should have some fundamental characteristics such as low price associated with good physical and mechanical properties.

The investigations carried out on PVC-natural polymer compositions prepared by melt blending of PVC matrix and natural polymer such as granular starch and cellulose have been done. Their behaviour when exposed to different environmental degrading conditions were examined.

Specimens of blends, as compression moulded and calendering films were prepared and their mechanical properties and structure were tested. The tensile strength and elongation of materials obtained depend on the natural polymer concentration in blends and the preparing conditions of compositions. The same specimens were submitted to degradation test under different environmental conditions: compost, liquid culture, activated sludge and isolated α -amylase enzyme.

The data obtained show as following:

- It is possible to obtain partially biodecomposable elastic material by melt blending of plasticized PVC with granular native potato starch and cellulose.
- The mechanical properties of plasticized PVC-natural polymer compositions are acceptable for such applications as packaging films, agriculture films, shopping bags etc.
- This material can be easily processed using typical equipment with no degradation during the processing step.
- Biodegradation of PVC-natural polymer films is evident on the surface of samples. Holes and cracks were observed. Intensity of surface damage depends on the type of biodegrading environment.

SOME NEW DIRECTIONS OF DEVELOPMENT OF POLYMERS AND PLASTICS

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1. A new liquid ,anhydrous reactive solvents (RS) from different compounds containing active hydrogen atoms and formaldehyde have been obtained. These RSs dissolve different condensation monomers (CM), especially melamine (Mel) also urea, phenol and their derivatives onto anhydrous solutions, liquid at temperature of dissolving, containing up to 100% polymerous substances. This kind of solution can contain up to 70% of Mel.. Dissolving CM have been bonded with synthesis and processing of polymers in the process of reactive forming, also for bonding of natural fibers (eg.wood).
2. By crosslinking plastified poly(vinyl chloride) with aliphatic amines under gelling conditions of PVC-E pastes a synthetic leather-like materials with higienic properties of natural leather has been obtained. Sorption and desorption of water vapour so crosslinked plasticated PVC reaches 30-40% (leather 10-100%). This PVC was obtained as poromeric film, which transmits water vapour but doesn't transmit liquid water. We have obtained also crosslinked PVC films which enhanced their surface in humid conditions and deminish it in dry conditions, similar to natural leather. This is the first polymer for LLM with higienic properties of natural leather.
3. New possibilities of obtaining ecological monomers, polymers and plastics, especially poly(methyleneurethanes) and poly(methyleneurethaneureas) from vegetable oil have been found in reaction with urea and formaldehyde.
4. From leather waste or possible sawdust as filler bonded with adhesive from same leather waste a water stable isolation - construction boards were obtained.

THERMOTROPIC MESOMORPHISM OF (2-HYDROXYPROPYL)CELLULOSE SYSTEMS – THE ROLE OF HYDROPHILIC AND LIPOPHILIC SEGMENTS

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Hydroxypropylcellulose (HPC) is a thermoplastic cellulose ether, soluble in water and in a wide variety of organic solvents. The scientific interest in this polymer was mostly related to its solution properties, due to a cholesteric liquid crystalline phase (LC) formed by HPC at high concentration. HPC in the solid state shows a complex morphology consisting of crystalline, amorphous and slightly ordered phases. This was conformed by a dielectric and mechanical loss processes in HPC [1]. Several studies appeared in the literature concerning the solid state properties and evidence were given that HPC exhibits LC behaviour even in the absence of solvent, at temperature higher then 130° C. Up to now, HPC was only interesting as a model for thermotropic polymer and is not commercial importance itself. This is because of its excellent solubility in water, alcohols and organic acids.

This report concerns our efforts to study behaviour of the systems based on HPC. Our interest have been directed towards: - (i) chemical modification of the molecular structure of HPC, -(ii) immobilisation of LC-organisation of HPC by the photopolymerization of vinyl monomer (acrylic or methacrylic acids) incorporated in system.

The series of HPC derivatives, two ester and cyanoethyl derivative were prepared, and the thermal, thermo-optical and mechanical properties (low frequency) were compared among them. The chemical modification of HPC macromolecules which is presented here leads to the liquid - crystalline polymers showing of thermotropic mesomorphism even at room temperature. The x-ray measurements and transition temperatures relation among investigated polymers can be explained with assumption that the microscopic phase separation takes place. In the crystalline and LC-states, the polysaccharide main chains (hydrophilic segments) tends to separate into network stabilised by intermolecular bonding, whereas aliphatic side chains (lipophilic segments) aggregate to form a complementary system held together by van der Waals forces.

In the field of the immobilisation of the LC-organisation of HPC, the polymer composites (blends) with poly(acrylic) and poly(methacrylic) acids were prepared. The immobilisation of LC-phase of HPC were achieved by a photopolymerization of acrylic (or methacrylic)

acid in the mechanically oriented lyotropic LC- solution of HPC in the acrylic acid. Particularly interesting is the network of non-mesomorphic polymer that is constructed in a oriented liquid environment of HPC. The liquid crystalline organisation of HPC is maintained in the polymer composite [2]. The composite of HPC-poly(acrylic acid) compared with the LC-mesophase of HPC to endure heat, solvents and mechanical deformation. The crosslinkage in the vinyl polymer by intermolecular hydrogen bonding plays a key role in preserving liquid-crystalline organisation of HPC. Finally, the immobilisation of LC-organisation of HPC macromolecules in the network of the polyacid strongly affected by hydrogen bonding, gives a homogenous composites in the macroscopic scale in contrary to non-miscible polymers: HPC and poly(acrylic acid).

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ZELFO – AN ENGINEERING MATERIAL FULLY BASED ON RENEWABLE RESSOURCES

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Starting point for the development of "Zelfo 2" was an intensive historical search for environmentally friendly materials, particularly in the area of the processing of papier mâché in the outgoing 19th century. Papier mâché, a material which had a high importance for consumer products at this time, was gradually replaced by Bakelite and other plastics.

Based on the knowledge of this historical investigation, extensive practical experiments were carried out so far with the goal to increase the internal linkage abilities of the cellulose fibers without addition of separate bonding agents. As result, materials with reasonable strength and stiffness could be produced. This cellulose fiber adherence is believed to take place exclusively via physical preparation processes without any chemical modification of the cellulose fiber. Thus it was possible to change the internal surface and the structural arrangement of the fibers in such a way that a completely new material named "Zelfo 2", also known as "Hempstone", could be formed. As raw material source for "Zelfo 2" cellulose containing wastes such as waste paper and old textiles, various plants such as hemp, flax, straw and reed (as raw fibers or as whole plant) or a combination of them can be used.

It is the purpose of this paper to describe the effects of these raw material variations and of processing parameters variations on mechanical properties (tensile strength, flexural strength, flexural modulus, charpy impact strength) and to interpret the results in terms of structure-property-relationships. Some of the results obtained so far are listed in Table 1 and compared to corresponding properties of several plastics (high-density poly(ethylene) (PE-HD), poly(vinylchloride) (PVC), phenolic resin) and Fasal (a thermoplastic wood based material).

Table 1 - Mechanical properties of hemp-based Zelfo 2 compared with common plastics and Fasal [1, 2, 3]

Material	Specific weight [g/cm ³]	Tensile strength [MPa]	Flexural strength [MPa]	Flexural modulus [MPa]	Charpy impact strength [kJ/m ²]	
					unnotched specimen	notched specimen
Zelfo 2	1.5	50...70	140	8 800	14	6
PE-HD	0.94...0.96	20...28 ^{a)}			no failure	8...18
PVC-U	1.4	55...70 ^{a)}	75...110		no failure	≥ 2
Phenolic resin, wood meal-filled	1.4	25	≥ 70	6 000...8 000	≥ 6	≥ 1.5
Fasal F134	1.4	25	45	5 800	4	

^{a)} Yield strength

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LIQUID CRYSTAL PHENOMENA IN CELLULOSE-NMMO-H₂O SYSTEM

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In the research programme realized there was carried out the analysis of the properties of the spinning solutions of cellulose in NMMO-H₂O system. Based on rheological properties of the cellulose solutions and measurements using FTIR and NMR methods it was confirmed that liquid crystals of cellulose appear in NMMO-H₂O system. Liquid crystal phenomena were observed not only in the high concentrated cellulose solutions in the stationary state but also in the cellulose solutions flow across spinneret hole. In this last case the existence of the liquid crystals is stimulated by pressure and ingredients.

SYNTHESIS OF REACTIVE POLYMERS AND THEIR APPLICATIONS TO COTTON FABRICS AS PERMANENT SIZE*

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Dextrin was first polymerized with acrylamide. The so obtained polymeric hybrid was converted to a reactive hybrid through methylation of its amide groups by react the latter with formaldehyde. On the other hand, poly(vinyl alcohol) was converted to a reactive form via its reaction with N-methylolacrylamide in alkaline medium. The two polymeric materials were then applied to cotton fabric with a view to achieve two objectives. The first is to prepare cotton fabric bearing permanent size. The second is to make use of these polymeric molecules in chemical finishing of cotton. In both cases the application involves acid catalyst besides, the application was carried out under different conditions including type and concentration of catalyst, curing time and the concentration of the reactive polymeric materials.

The treated fabrics were monitored for strength properties, size add-on, and durability in addition to crease recovery in case of the finished fabric.

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CONCEPTION OF PROCESSING OF POROUS, FIBROUS, OIL & POLYMER WASTE INTO DISSIPATIVE & BUILDING STRUCTURES

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It is known that dry, fibrous, polymer, oil industrial waste can be efficiently used for making the dissipative and building structures. We have come to the conclusion that the said waste represents the full collection of the raw materials for all components of such structures including bindings, fillings, intermediate phases with the exception of dye stuff.

Our new production techniques exclude the use of harmful chemicals. These technologies are based on putting in practice the mechanical and thermodynamical methods of transformation of non-recyclable waste into composites, structure materials, other goods.

On the base of our resource saving techniques we have developed the efficient little metal requiring complete production lines to process waste into wares. Employment of these techniques could solve a complex of social, economic and environment problems.

The outcome of our long investigations is the complete program of manufacture of up to 200 items of consumer goods for various purposes – for construction, for heat and sound absorption, noise insulation, roofing, sealing, anticorros, lubricants etc.

Nanostructured Materials, Nanoparticles and Nanocomposites

Invited lecture

**PROCESSING ASSISTED SELF-ORGANIZATION AS A PARADIGM
FOR INTRINSICALLY POLAR POLYMER FILMS**

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Electrically poled, chromophore-bound, polymer films which are macroscopically noncentrosymmetric (i.e., bulk polar order) are of interest for electro-optic switches and signal modulators for high bandwidth data processing. Second order nonlinear optical activity requires a polar structure, which is normally achieved by applying an electric field to a chromophore-containing polymer. An alternative to the poled polymer approach that avoids high temperature processing and high electric fields is the use of an intrinsically polar organic solid, but such structures are uncommon. This presentation explores two approaches to achieve intrinsically polar structures in polymer films.

The first method utilizes the Langmuir-Kuhn method of film deposition. Syndioregic accordion polymer architectures for LBK deposition of complementary bilayers are described with the objective of producing *intrinsically* polar polymer films. The polymers designed for polar bilayers have a syndioregic mainchain NLO polymer topology in which hydrophilic and lipophilic bridging groups are located on alternating bridging sites between the chromophores in order to bring about polar self-ordering at an air-water interface. These multilayer thin films have second order nonlinear optical properties that are stable at ambient temperature in the absence of oxygen. However, these accordion polymers have rather low glass transition temperatures (75 to 95°C) and are thus impractical for applications.

A second approach has been devised to build up polar films that are more environmentally stable. By this method, polymers ionically bind at the gas/liquid interface to produce a bilayer polymer salt which may be subsequently be transferred to a solid substrate in a highly uniform manner with each added bilayer. A linear increase in UV-Vis absorbance and a quadratic dependence of SHG on increasing film thickness is observed.

A third approach utilizes alternating polyelectrolyte deposition (APD), a layer-by-layer technique for the formation of polymer films. Film deposition is achieved by alternately immersing a substrate in aqueous solutions of a polyanion and a polycation. APD allows precise control of the overall film thickness that through automated processing may exceed a thousand layers. In this work, the formation on hydrophobic glass of acentric APD films with high thermal stability was demonstrated. The high thermal stability of the polar order makes the APD films potentially attractive for device applications.

Invited lecture

POLYMER NETWORKS FROM PRECURSORS OF VARIOUS ARCHITECTURES

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PRECURSORS OF POLYMER NETWORKS

Precursors of polymer networks are prepolymers of various architecture carrying reactive groups which participate in bond formation during the crosslinking process. The current architectures are telechelic polymers, functional copolymers, stars or combs, functional microgels, dendrimers, hyperbranched polymers, etc. Stars, microgels, dendrimers and hyperbranched polymers belong to the group of precursors of compact architecture. They have the advantage of low viscosity compared to linear precursors of the same molecular weight and functionality. Modern synthetic methods make it possible to arrange monomer units in the desired sequential order in functional copolymers. Specific arrangement of the functional groups in the precursors, unlike in simple monomers or telechelic polymers, affect the reactivity and network formation. In this contribution, some features of architecture control and their effect on network formation are discussed and examples of functional copolymers, functional stars, and hyperbranched polymers are employed. Modeling of reactivities and network formation are emphasized.

FUNCTIONAL COPOLYMERS

The effect of the type of neighbouring unit on reactivity of functional groups during the crosslinking reaction is typical of functional copolymers. The network build-up characterized by an increase in molecular weight, gel point conversion, decrease in sol fraction and increase in the degree of crosslinking, is controlled not only by the number of functional monomer units per precursor molecule but also by sequential arrangements of functional (A) and non-functional (B) monomer units (e.g. random (BAABBABBBAAA) vs. block (AAAAAABBBBBB) copolymers). In addition, the neighboring reacted functional group (X) has a different effect on the reactivity compared with the unreacted one (A). Theoretically, the neighbour effect was treated by formulating kinetic transformation equations for triads. They describe the transformation rate of functional group A into product X affected by neighbours while keeping the original degree-of-polymerization distribution of the primary chains intact. To describe the formation of

branched and crosslinked structures by reaction with a crosslinking agent, the theory of branching processes was used. The transformed distribution of A-X-B primary copolymer chains was obtained by the matrix method for generation of finite Markov chains. Experimentally, the neighbour effect was investigated for crosslinking with diamines of random and block copolymers of glycidyl and butyl methacrylates. However, it was observed that association in some solvents affected the kinetics.

FUNCTIONAL STARS

Functional stars have either simple (arms issue from one branch point) or dendritic structure. They are usually smaller than typical dendrimers. The functional groups located at the extremities have the same or different reactivity. As the desired functionality can be adjusted by blending stars with different number of functional groups, and the reactivity can be adjusted by blending of stars of different reactivity, the effect of blending on performance has been an important issue.

The theory has predicted and experiments have confirmed that the blends always exhibit an earlier gelation and a steeper viscosity build-up than the corresponding monodisperse systems. Dendritic stars contribute more to the crosslinking density than simple stars of the same functionality, but they exhibit the same critical conversion and gelation time.

HYPERBRANCHED POLYMERS

Hyperbranched polymers carrying reactive A and B groups are obtained by reaction of BAX ($x = 2, 3, \dots$) monomers (A reacts with B) and are characterized by distributions of degrees of polymerization and shapes. There exist several ways of modifying these distributions such as introduction of a core (A_y monomer), using monomers with A groups of different reactivity or exhibiting substitution effect, and controlled addition of monomers. Under ideal conditions, each acyclic molecule contains one B group. The presence of the B group makes cyclization possible and rings of varying sizes are formed. The formation of cycles was modeled theoretically and confirmed experimentally for poly [2,2-bis (hydroxymethyl) propanoic acid]. Cyclization strongly affects the distribution of the degrees of polymerization.

The functionality of higher-molecular-weight hyperbranched polymers is usually too high to use them as precursors of polymer networks; the gelation conversions are too low. Moreover, some hyperbranched structures are too rigid. These disadvantages can be circumvented by a partial reaction of the end groups with a monofunctional component and by incorporation of a softer bifunctional component of AB type.

The kinetics of the crosslinking reaction and the network build-up are affected by limited accessibility of some of the reactive groups due to steric hindrance.

Invited lecture

**POLYMER-INORGANIC NANOCOMPOSITES
FOR OPTICAL APPLICATIONS**

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If the diameters of inorganic particles embedded in polymers are below 50-100 nm in at least one dimension, the resulting materials are called nanocomposites. Such systems are characterized by a strongly reduced scattering of light compared to composites with particles of larger dimensions. Nanocomposites are, therefore, particularly suited for optical applications. For example, the refractive index of polymers, a key feature in optical applications, can be greatly enhanced or reduced by incorporation of small inorganic particles with extreme refractive index. In another example, a thin layer of an optically transparent nanocomposite layer in the surface region of a polymer was used to absorb UV radiation. While typically the inorganic particles or particle agglomerates in the polymer nanocomposites described so far were randomly distributed, we have prepared recently nanocomposites in which the inorganic particles are preferentially oriented uniaxially in parallel strings of particles. Such materials change their color in polarized light observed at different angles between the polarization axis of the transmitted light and the orientation axis of the particle strings. Such materials are, in principle, suited for color polarizing filters which could be used, e.g., in liquid crystal displays.

*Invited lecture***NANOSCALE PHOTOVOLTAICS
IN ORGANIC THIN FILMS AND CRYSTALS****Denis Fichou¹, Fabrice Charra², and Alexandre Gusev²**¹ Laboratoire des Matériaux Moléculaires, C.N.R.S., Thiais, France² DRECAM, CEA Saclay, Gif sur Yvette, France

Renewable energies such as solar photovoltaic electricity are a worldwide key issue of the next decades. An alternative to the expensive silicon-based photovoltaic technology is the use of organic semiconductors. These last few years, a number of organic molecules and polymers having intense visible absorption and efficient transport properties have been used to design photovoltaic solar cells. In order to optimize the efficiency of these planar devices, it is crucial to control the relationships between the morphology of the organic layers and their electrooptical properties at the nanoscopic level.

We demonstrate here that the tip of a scanning tunnelling microscope (STM) can be used to design a nanoscale photovoltaic cell when the sample is an organic semiconductor. This system can be assimilated to a metal-insulator-semiconductor (MIS) junction where the STM tip is the metal, the air gap the insulator and the organic sample the semiconductor. We show in particular that upon illumination by a He-Cd laser beam, sexithiophene (6T) and octithiophene (8T) single crystals deposited on top of a semitransparent conducting ITO substrate or organized layers on a gold(111) surface generate a tunnelling photocurrent. Note that both 6T and 8T compounds are efficient organic semiconductors whose transport and optical properties have been extensively studied over the last ten years [1]. We observe a neat rectifying I/V characteristic of the junction, the air gap width being controlled by the tip height at the Å scale. Importantly, the weak photocurrent produced by the organic nano-MIS-junction allows to visualize simultaneously the surface morphology and the short-circuit photocurrent. The computerized combination of both signals results in a 3D-mapping of the 6T and 8T samples where regions of high/low photocurrent perfectly correlate those of defect-free/full morphology respectively [2]. We reveal in particular the direct correlation between the steps-and-terraces crystallographic profile and that of the photocurrent density.

In conclusion, light-assisted STM spectroscopy thus constitutes a powerful tool to probe the nanoscale origin of the photovoltaic effect in organic semiconductors and should allow considerable improvements of the efficiency of large-area organic solar cells.

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Invited lecture

NANOSTRUCTURED MATERIALS FROM RADially LAYERED POLY(AMIDOAMINE-ORGANOSILICONE) (PAMAMOS) COPOLYMERIC DENDRIMERS

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Radially layered copolymeric poly(amidoamine-organosilicon) (PAMAMOS) dendrimers which consist of hydrophilic polyamidoamine (PAMAM) interiors and hydrophobic organosilicon (OS) exteriors are an unusual family of nanostructured macromolecules in this new class of molecular architecture. The copolymer concept has proved to be central to tailoring versatile new structures with conventional linear, randomly branched and cross-linked polymers but so far has been little exploited in the otherwise rapidly expanding field of dendritic polymers. PAMAMOS dendrimers can be prepared by several different synthetic methods [1] to provide a variety of different structures, containing: (a) different numbers of layers of constitutive branch-cells, (b) different compositions of the OS branch cells and (c) different reactive or inert end groups. The two synthetic approaches we have most exploited are siliconization of amine-terminated, ethylenediamine core PAMAM dendrimers either by the Michael addition reaction of silicon-containing acrylates or haloalkylation with various silanes and siloxanes. These structures have been characterized with a wide range of bulk and surface analytical techniques including ¹H, ¹³C, and ²⁹Si NMR, DSC and TGA, GPC, MALDI-TOF and Electrospray MS, surface tension and Langmuir trough studies, contact angle, SEM(EDS), AFM and XPS.

Derivatives of these dendrimers with inert trimethylsilyl-terminated groups may be viewed as globular, covalently bonded “inverted micelles” with unusual surface properties [2]. They form liquid-like spread films on water capable of sustaining much higher surface pressures than linear polydimethylsiloxane. Values of over 50 mN/m are attained, providing a marked example of the impact of macromolecular architecture on surface properties of organosilicon-containing polymers. Surface areas from these Langmuir trough studies are in good agreement with expected PAMAMOS dendrimer sizes from dilute solution viscometry and molecular modeling. Increases in area occur both with increasing degree of organosilicon substitution of the parent PAMAM dendrimer surface groups and with increasing PAMAM generation number.

Derivatives of these dendrimers with reactive methoxysilyl-terminated groups are excellent precursors for unique nanostructured tractable dendrimer-based materials [3]. These dendrimer-based networks consist of nanoscopic domains of hydrophilic PAMAM with

well-controlled, predetermined size and shape distributed evenly in a continuous hydrophobic organosilicon matrix. They can be conveniently shaped into elastomeric films, coatings and membranes. These new nanostructured materials show exceptional complexation abilities towards inorganic electrophiles and offer unique opportunities for nano-technology of semi-permeable membranes, molecular “sponges” and “reactors”, nanoscopic inorganic-organic composites and functional protective coatings for a variety of substrates.

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Invited lecture

**NANOSCALE CHEMISTRY AND PROCESSING
OF MULTIFUNCTIONAL COMPOSITES
FOR NANOPHOTONICS AND BIOPHOTONICS**

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Nanophotonics deals with optical science and technology at nanoscale. In this area our effort is in three directions: 1) Nanometer Confinement of Matter 2) Nanometer Confinement of Radiation and 3) Nanoscale Photo Processes for Nanofabrication. However, the present talk will focus on *Nanoscale Chemistry and Processing to Prepare Nanostructured Photonic Materials*.

Nanostructured materials and composites offer opportunity to tailor the nonlinear optical response and optical communication for controlling and broadening the range of photonic function. At the molecular level, one can utilize nanoscale synthesis to prepare structures with a control of optical band gap or conjugation length as well as to make inorganic: organic hybrid structures. We have utilized nanoscale synthesis in reverse micelle nanoreactors of controlled sizes for this purpose. In another approach, we have utilized chemistry and processing in nanopores of sol-gel processed glass to prepare nanoscale multiphase composites for multidomain lasing, optical power limiting, and other photonic functions.

Biophotonics is a newly emerging field describing the application of light wave technology to medicine and dentistry. The talk will cover our efforts to develop nanoscale fluorescent probes for imaging of processes both at cellular and tissue levels.

Invited lecture

**COLLECTIVE OPTICAL AND MAGNETIC PROPERTIES
OF NANOCRYSTALS ORGANIZED IN 2D SUPERLATTICES**

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The lecture will be divided in two topics:

1. We will describe the collective optical properties of silver nanoparticles organized in 2D and 3D superlattices. The optical spectra are compared with both polarized and unpolarized light. Under p-polarized light, a new high energy peak appears which is interpreted as a collective effect, resulting from the mutual interactions between particles. We support this conclusion from numerical calculations performed on finite size clusters of silver spheres
2. When cobalt nanoparticles are arranged in 2D superlattices, magnetic collective properties are observed. This will be compared to that obtained for same particles dispersed in a solvent.

Invited lecture

NANOPARTICLES FOR CERAMIC AND NANOCOMPOSITE PROCESSING

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The synthesis for the fabrication of nanoparticles through a sol-gel-related precipitation technique has been developed. By appropriate surface modification, the nanoparticles can be isolated to dry fully redispersible powders, hydrothermally treated in order to improve crystallization, or they can be in-situ redispersed in polymeric or ormoecer matrices. Using this approach, ceramic processing techniques as well as routes for the fabrication of polymer matrix nanocomposites have been developed. For the synthesis of stable nanoparticle suspension, which are a prerequisite for the materials fabrication, the ζ -potentials have been tailored by appropriate surface modification, or surface modification has been used to reduce the interfacial free energy between the particle and the matrix.

A series of materials for practical use have been developed, such as transparent nanocomposite hard coatings, gradient coatings with low surface-free energy, graded index materials or optical interference coatings for IR-reflecting or antireflecting purposes. In the paper, a survey over the chemical processing route of nanostructured materials and a series of applications is given.

Invited lecture

FROM MICROCRYSTALS TO NANOPARTICLES IN HETEROGENEOUS POLYMERS

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Since more than twenty years we are interested in microcomposites consisting of micro- or nanocrystals, as well as of nanoparticles, in polymeric matrices. It seems necessary to characterize briefly nanostructural materials. All nanostructural materials have following features: they consist of atomic domains, grains layered phases, and they are usually confined. Significant fraction of them is associated with interfacial environment and with interaction between the domains. Increasing interest in nanostructured materials is coming from anticipation that their properties will be different or superior to the conventional materials. Wide studies on nanocomposites, developing new scientific and technological problems, have shown that it is possible to engineer new material varying their constituents (domains) and the manner in which they are assembled.

In this way one can obtain advanced materials with controlled: chemical, optical and mechanical properties and in consequence – materials for new application. Depending on topology and dimensionality, structure of nanocomposites can be extensively changed, even for two component materials.

It is not possible here to enumerate all differences in preparation methods; however, they strongly influence the final product. One has to distinguish dry techniques (various type of deposition in vacuum) and “wet” techniques. These “wet” techniques were an inspiration for development of colloidal chemistry, L.B. method, as well as self association of amphiphilic molecules.

Many important properties of micro- and nanocomposites depend on the volume, order and dispersion of the additives. The structure of microcrystalline nanophase must be stable.

There is also a possibility of nanostructured systems formation by polymerization of an appropriate monomer in the presence of nanosized additives.

These both techniques will be discussed in some details.

One way to prepare micro- and nanocomposites consists in crystallization in situ of additive e.g. CT complexes by the evaporation of solution in common solvent for polymer. In this way one can obtain a continuous network of crystallites responsible for magnetic, optical and particularly electrical properties. Using a variation of this method, at first elaborated in our laboratory is possible to obtain isotropic, surface and anisotropic conducting systems. Due to small amount of additives and their connectivity those materials are called reticulate doped polymers. Highly conducting films with BEDT-TTF were obtained using modified reticulate doping technique. Recently we have developed a method in which oxidation of the donor with iodine and the crystallization of the resulting salt take place in situ of the swollen polymer. Identification of polyiodide crystallization network is difficult. The conductivity of separate microcrystals exhibit metallic character with a maximum at about 100 K. Stability of the films is good. Attempts have been made to transform the crystalline phases by annealing in order to obtain superconducting β^x phase of $(\text{BEDT-TTF})_2\text{I}_3$ will be described.

Crystallization method in situ of polymer matrices of TCNQ salt and other substances leads to materials showing nonlinear properties.

Methods of preparation of polymer composites with super paramagnetic nanoparticles are briefly reviewed. Multicomponent polymer systems with nanoparticles of metal oxides can be exhibit besides of good magnetic properties and transparency also good adhesion (polymers of various type and copolymers) and film forming properties. Our studies on selected system poly aniline/iron oxide particles lead us to explain why the calculated saturation magnetization is different from that which is measured.

The presented results show that some problems of the field of micro- and nanocomposites are resolved but we hope that the present studies will throw some light on these fields but also strongly indicate that there are many questions open in the field of nanostructured materials both in science and practical applications.

Invited lecture

**THE ROLE OF COMBINATORIAL CHEMISTRY
IN IDENTIFYING STABLE, VOLATILE COMPOUNDS**

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Many modern applications rely on components with electronic materials. Most of these devices function with dopant atoms to tailor the electronic properties. One traditional device structure growth technique is chemical vapor deposition (CVD). Dopants are incorporated into thin film deposits in CVD by employment of gaseous compounds. Having stable, volatile precursor molecules often presents a challenge to the synthetic chemist. Recently, we have developed a rapid combinatorial synthesis approach, and, in parallel, a new characterization technique for selected examples of this class of compounds.

*Invited lecture***PHOTOCHROMIC MOLECULES AS BUILDING BLOCKS
IN LANGMUIR-BLODGETT FILMS****Juliusz Sworakowski**Institute of Physical and Theoretical Chemistry,
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Attempts of incorporating photochromic molecules into Langmuir-Blodgett films aim at obtaining photoresponsive thin films having well defined geometric parameters and a good organization of photoactive species. Potentially, films fabricated in such a way can be employed as high-density optical storage elements or command surfaces' for liquid crystalline cells [1]. The technique of depositing Langmuir-Blodgett (LB) films consists of three steps: molecules are spread on the surface of a subphase (usually high-purity water), compressed to form an organized monolayer (Langmuir film), and then transferred onto a solid substrate. In favourable conditions, the procedure can be repeated several times allowing one to obtain multilayer structures. Fabricating good-quality LB films containing photoactive molecules may prove difficult as often the compression does not lead to ordered Langmuir monolayers or the transfer of the monolayers onto a solid substrate results in ill-organized film. One may improve the deposition of photoactive molecules by mixing them with 'supports' - usually neutral fatty acids or their salts. Alternatively, one may deposit polymers containing photoactive side groups. In both cases, a question arises about the phase status of the films obtained in such a way and their organization.

Molecules deposited using the LB technique should be amphiphilic, i.e., they should contain a hydrophilic 'head' and a hydrophobic 'tail'. Among molecules used as photoactive components of LB films, functionalized spiropyrans and azobenzenes have been often used [1]. Results obtained on the latter group are reviewed in the present contribution.

The photoisomerization of azobenzene derivatives in solutions and polymer matrices has been extensively studied and commonly accepted models exist [2]. The situation in organized thin films is, however, far from being understood in detail. In particular, details of the packing of molecules may crucially influence the photochemical activity of LB films. Moreover, a possibility of protonation of the $-N=N-$ moiety should modify the energetics of the isomerization. These problems will be discussed in the contribution.

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Invited lecture

ELECTRIC CONDUCTING COATINGS MADE FROM REDISPERSABLE CRYSTALLINE NANOPOWDERS

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Electrical conducting films deposited on plastic and glass substrates are today widely used as transparent electrodes, heat reflectors, antistatic and electromagnetic shielding. We shall first present a wet chemical concept [1,2] for the preparation of crystalline nanoscaled powder which can be fully redispersed in a solvent such as alcohol or water. The synthesis of the particles is carried out at temperature $< 200^{\circ}\text{C}$ in a solution by a controlled growth reaction (pressure and temperature) using metal chlorides, nitrides or acetates as precursors. The aggregation of the particles is avoided by in-situ modifying the powder surface with bifunctional organic molecules. The process has been applied for the preparation of $\text{In}_2\text{O}_3:\text{Sn}$ (ITO), SnO_2 (TO) and $\text{SnO}_2:\text{Sb}$ (ATO) particles. ITO powder is redispersable in ethanol or water at a $\text{pH} < 5$ with solid contents up to 40 wt %. The colloidal suspensions are stable (no precipitation) at room temperature during at least 1 year. ATO powder is only redispersable in water at $\text{pH} > 8$ and the suspensions are also stable (no precipitation) at room temperature during at least 1 year. The redispersed particles consist of single crystallite (cassiterite structure for TO and ATO, cubic In_2O_3 structure for ITO) and their average size is 7 ± 1 nm for TO, 4 ± 1 nm for ATO (5 mole % Sb) and 15 ± 1 nm for ITO (8 mole % Sn). The size distribution is monomodal. (figure 1)

Single layers with thickness up to 200 nm (ATO) and 400 nm (ITO) have been deposited on float glass, borosilicate or fused quartz substrates using the dip or spin coating processes (size up to 30 x 45 cm). The resistivity of the layers strongly decreases with the sintering temperature. Typical lowest values are $\rho = 1,7 \cdot 10^{-2} \Omega \text{ cm}$ for ATO (550°C) and $\rho = 1,0 \cdot 10^{-2} \Omega \text{ cm}$ for ITO (900°C). The resistivity of ITO coatings can still be reduced after annealing in N_2 atmosphere performed at $T > 300^{\circ}\text{C}$. Values as small as $\rho = 3,4 \cdot 10^{-3} \Omega \text{ cm}$ are obtained for coatings sintered at 900°C (figure 2). The resistivity of as fired ATO and ITO coatings is stable. It however increases with time for ITO in the reduced state and reaches a constant value ca. half of that obtained without annealing after 40 days. The resistivity of fired coatings remains unaltered under continuous storage at high temperature, up to 600°C for ATO and 900°C for ITO. The sheet resistance of the coatings is reduced linearly by repeating the deposition process (multilayer coatings). All coatings present a high optical transmission ($> 90\%$) in the visible range.

Plastic (polycarbonate) substrates can be coated using the ITO nanoparticulate sols chemically modified by addition of organo functionalized silanes. These additives allow to polymerize and harden the layers thermally (130°C) or by UV irradiation at room temperature. The coatings resistivity is however higher ($\rho \cong 10 \Omega \text{ cm}$) corresponding to a sheet resistance of ca. $250 \text{ k}\Omega_{\square}$. Such coated substrates present excellent antistatic properties.

Antiglare conducting ITO coatings have also be produced on glass substrates by spraying at room temperature nanoparticulate sols chemically modified by addition of small amount of alkoxy silanes. After sintering the coatings exhibit a rough surface ($R_a \cong 200 \text{ nm}$) consisting of random and homogeneous conducting particles and voids with size varying from 100 to 300 nm. Such configuration considerably reduce the glare of the substrates down to ca. 70 gloss units.

Antireflex antistatic (ARAS) coatings have also been obtained as a 2 layers interference system (HL configuration) by depositing a thin silica layer (low refraction index L) on top of a thick ATO or ITO coatings (high refraction index H). The reflectivity in the visible range can be reduced down to ca. 1 %.

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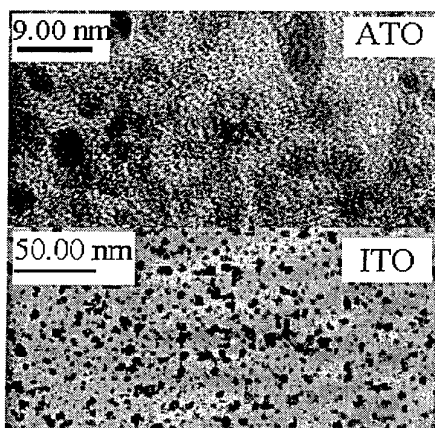


Fig. 1 HRTEM picture of ATO and ITO redispersed powder

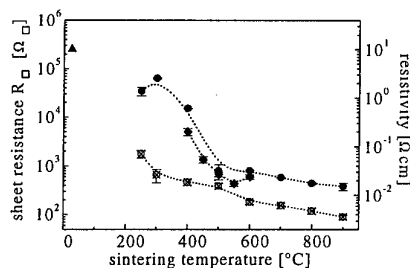


Fig. 2 R_s and ρ of 400 nm thick ITO and ATO coatings vs sintering temperature: ATO (◆), as fired ITO (□), Y annealed ITO, π ITO on PC

Invited lecture

**CONTROL OF OPTICAL PROPERTIES USING VARIOUS
NANOSTRUCTURED MATERIALS: DENDRIMERS,
PHASE-SEPARATING BLOCK COPOLYMERS,
AND POLYMER MICROSPHERES**

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Light harvesting dendrimers contain organic chromophore and trivalent rare ion cores have been prepared. Such structures effectively reduced quenching of rare earth ion luminescence associated with self- and ligand quenching. Moreover, by appropriate chromophore incorporation in various generations, efficient light harvesting over the UV to infrared spectral regions has been achieved. Design of phase separating block copolymers, containing chromophoric blocks with chromophores coupled in a head-to-tail manner, has been carried out so that acentric overall assembly occurs driven by enthalpic interactions. Finally, the production of photonic bandgap materials using polymeric nanostructured materials as templates is discussed.

Invited lecture

SYNTHESIS OF MESOPOROUS SILICATE BY TEMPLATING OF AMPHIPHILIC POLY(ETHYLENE GLYCOL-BLOCK-PROPYLENE GLYCOL-BLOCK-ETHYLENE GLYCOL)

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Synthesis of ordered porous materials by using templating of surfactants have attracted much interests due to their wide applications in catalytic reaction, separation and purification. For templating, most of studies focused on the low molecular weight surfactant such as cetyltrimethylammonium bromide(CTAB)^[1-3], which easily form aggregates with globular, cylindrical and hexagonal shape in solution. On the other hand, amphiphilic block copolymers in the aqueous or other solutions have ability to self-organize and invoke well-ordered micelles or liquid crystal^[4,5], around which the silicate source condense or chemicals attract. This process hints that some macromolecular architecture can be employed as template in the synthesis of porous materials at different length and time scales. Thus, exploiting novel materials and applications is possible. However, the use of amphiphilic block copolymers to prepare self-assembled porous materials is seldom^[6,7].

In this work, the well-ordered porous silicate was synthesized by templating of poly(ethylene glycol – block- propylene glycol – block – ethylene glycol)(denote PEG-PPG-PEG).PEG-PPG-PEG with two different average molecular weights (5800g.mol⁻¹ and 8400g.mol⁻¹,respectively) and different length of EG and PG block were used to prepare the aqueous solution of micelle at 18°C under moderate stirring for 4-8hr, from which white precipitated products formed within 1-5min after adding inorganic precursor TEOS into template solution. The age time of white solid in solution is from 12hr to 7 days. Solid product were allowed to be washed by de-ionized water, filtered by membrane, air-dried at room temperature and calcined in air at 773K for 6hr to remove template. Samples were prepared under various conditions such as content of copolymer, reaction or aging time and temperature, composition, with or without calcining and so on. The pore size and shape, effective pore size of samples were determined by using powder x-ray diffraction (XRD) and the N₂ adsorption isotherm (BET).Thermal properties were characterized by using thermogravimetry dynamic analysis (TG-DTA).

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ORGANIC NANOCRYSTALS IN SOL-GEL GLASSES: A NEW TYPE OF MATERIAL FOR PHOTONICS

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In this work, we have designed a new type of composite materials for optical applications: organic nanocrystals embedded in sol-gel glasses. The nanosized control of crystallization allow us to obtain optical grade samples with very high (>50wt.-%) concentrations of active molecules. These materials not only combine the unique optical properties of organic molecules with those of inorganic materials (high stability, wide transparency range), but also the advantages of crystals (size effects, increased photostability), with those of amorphous phases (convenient processing and shaping).

The nanocrystallization is obtained by an instantaneous nucleation followed by a controlled growth of the nuclei. In this process, the gel viscosity reduces the growth rate and avoids coalescence while gel pores act as nanosized growth reactors. The process is based on the control of the nucleation and growth kinetics of the organic phase. For bulk samples, monodisperse sizes as small as 20nm have been obtained in this work. We have extended this method to the preparation of stable organic nanocrystals in thin films gel-glasses using the spin coating technique.

Currently, we have succeeded in designing nanocomposite materials with molecules selected for their non linear absorption at visible wavelengths (for optical power limiting applications) and their solid-state fluorescence (for solid-state dye laser applications). We will also report on progress towards the design of new materials with extended optical properties .

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NANOPOROUS ORGANIC SOLIDS FROM POLYDIACETYLENE CHARGE-TRANSFER COMPLEXES

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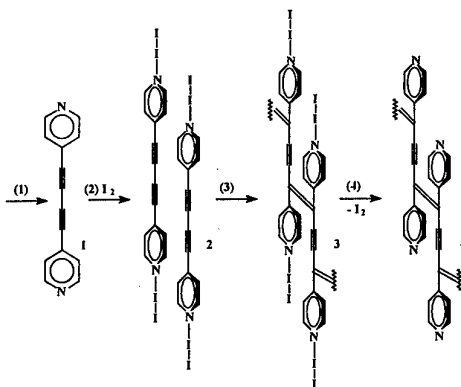
CHARGE TRANSFER COMPLEXES WITH NITROGEN HETEROCYCLES

For the past few years, we have been exploring the use of iodine and other Lewis acceptors for the manipulation of the solid state structure of heterocycles.^{1,2} A variety of nitrogen heterocycles have been used to form crystalline charge-transfer complexes with these acceptors. The charge-transfer interaction is relatively strong (~10 kcal/mol), highly directional and acceptors which can coordinate up to four donors are readily available. Controlled thermolysis of the solid leads to removal of the relatively volatile Lewis acid, collapse of the original crystal lattice and formation of a polymorph of the original heterocycle. Thus, we have used the charge-transfer interaction to control the ultimate solid state structure of organic compounds. In some cases, transformations between polymorphs can be accomplished entirely in the solid state.³

NANOPOROUS SOLIDS

Very recently, we have extended this concept towards the construction of nanoporous solids by preparing charge-transfer complexes between Lewis acceptors and heterocycles containing diacetylene or diolefin substituents. Both classes of compounds contain members able to “topopolymerize”, *i.e.* to undergo single-crystal to single-crystal polymerization.

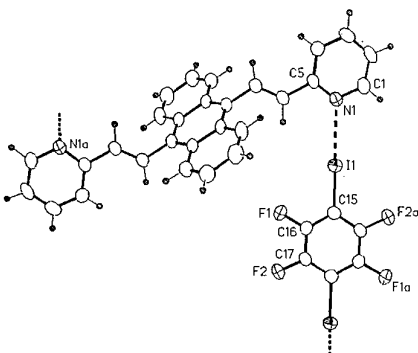
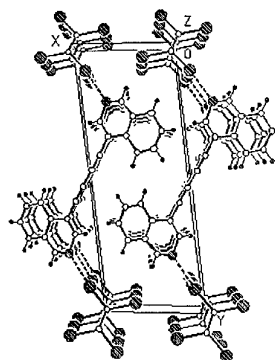
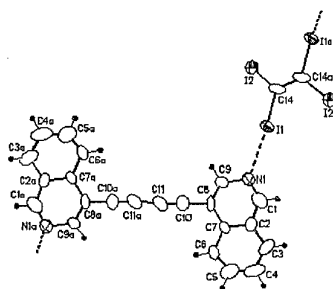
The scheme to the right illustrates how polymeric crystalline solids containing well-defined, electron-rich voids and channels might be constructed. In the first step, a diacetylene is prepared by well-established synthetic routes. We have successfully prepared a number of



previously reported and new compounds in this manner. Using synthetic strategies previously developed in our laboratories, we have isolated and characterized charge-transfer complexes of several of the diacetylenes (step 2).

Step 3 is the most critical step of the synthesis. Topopolymerization will only occur when the diacetylenes stack within certain critical geometric parameters. Lewis acid complexation can alter packing distances and angles, helping or hindering polymerization. The crystal engineering of polymerizable complexes such as 1,4-bis(4-isoquinolyl)buta-1,3-diyne:tetraiodoethylene (right) requires an understanding of not only charge-transfer interactions, but also other intermolecular interactions in the system.

Step 4, the removal of the guest has not yet been attempted and will not be discussed here.



Diolefin-base non-porous solids may be constructed by a similar route. While the polymerization mechanism is quite different from that of the diacetylenes, very high molecular weight polymers can be formed via 2+2 cycloadditions of the olefin moieties. This vinyl pyridine derivative of anthracene coordinates well with tetrafluorodiodobenzene. As with the diacetylenes, there are strict geometrical requirements for the successful polymerization of diolefins. A discussion of supramolecular structure

optimization strategies will be presented along with our latest results in preparing and characterizing polymeric charge-transfer complexes.

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POLYMER ELECTROLYTES DERIVED FROM HIDROXIETHYLCELLULOSE/POLYETHER NETWORKS

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Polysaccharides like cellulose and its derivatives can be used in polymer electrolytes due to their aptitude to generate thin films. This paper reports the reaction of hidroxyethylcellulose with oligoether-based diisocyanates. The resulting networks were investigated by differential scanning calorimetry and infrared spectroscopy.

INTRODUCTION

The understanding of fundamental features on polymer electrolytes [1,2], led to the optimization of the conductive of POE-based networks, with its structure lightly perturbed due to the previous reaction with oligoether diisocyanates. After reaching a good achievement in terms of stable and highly conductive polymer electrolytes, the possibility of improving thin-film properties (in order to optimize the elaboration of thin devices) showed itself as an interesting problem to studied. In this field cellulose and its derivatives are very attractive because of their film forming and mechanical properties and also for the reason of their abundance on nature. Some preliminary tests were published [2-4] reporting the good mechanical and electrical properties while improving the possibility of casting films. The systematic study of the properties of the hidroxyethylcellulose (HEC) based network will contribute to the optimization and understanding of the conductivity of polysaccharides network.

EXPERIMENTAL

Five samples of commercial HEC (gently given by UNION CARBIDE DO BRASIL) were used in this work differing in degree of polymerization (DP) degree of substitution (DS) and degree of molar substitution (MS). This properties were determined using various techniques already reported [5-7]. PEO-based di-oligoisocyanates were synthesized from the corresponding commercial Jeffamine, following previously developed procedure [8]. The isolated products gave the expected spectroscopy characteristics and were stored in the absence of moisture. The condensation reactions were made in DMAc solution at room

temperature in the presence of traces of dibutyltin dilaurate as catalyst. Membranes were obtained by pouring the viscous solutions in a mould immediately after mixing the reagents. The materials obtained were characterized by DSC and by infrared spectroscopy.

RESULTS AND DISCUSSION

Looking at the properties of the HEC utilized (showed in table I) we can observe that DS and MS are linearly dependent. In this way, we proposed the study of the properties of the networks as function of these parameters. In this sense, the percentage of NCO functions introduced in the polysaccharide chain was determined to be constant and equal to 60%, in respect to the OH functions present in the chain. The DSC curves for all networks are similar and the glass transition temperature (T_g) for the films are reported in table 1. It can be observed T_g going from -50°C , for films with diisocyanate of poly(ethylene oxide) (DPEO), to -35°C for films with diisocyanate of poly(propylene oxide) (DPPO). The comparison of T_g for a series of networks of different HEC with the same isocyanate shows that there was no significant change on this property. However, we can observe that T_g is higher for networks formed with DPOP. As a conclusion, the glass transition temperature, an important property for the conduction phenomenon, is function of the isocyanate aggregated to the polysaccharide chain and not to the characteristics of this macromolecule. The obtained FTIR spectrum showed that reaction between diisocyanate and polysaccharide occurred suggesting a formation of a network structure.

Table 1: Properties of the HEC utilized and of the networks formed after its reaction with isocyanates

HEC	MS	DS	DP	T_g	
				DPEO	DPPO
QP09H	1.22	0.75	260	-54	-36
QP300H	0.58	0.34	850	-47	-35
QP4400	1.35	0.88	1840	-48	-35
QP15MH	1.72	1.01	2450	-52	-33
QP30MH	0.91	0.54	2480	-52	-34

CONCLUSION

The progressive improvement of the overall performance of cross-linked polymer electrolytes has advanced one step further by the study of the properties of the networks using hydroxyethylcellulose grafted with oligoether-based isocyanate. The reaction provided a good film-forming network where the glass transition temperature is a function of the type of isocyanate introduced in the polysaccharide chain.

ACKNOLOGMENTS: FAPESP, UNION CARBIDE DO BRASIL, PRÓ-REITORIA USP

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TRANSPORT AND MECHANICAL PROPERTIES OF POLYANILINE-POLY(METHYLMETACRYLATE) BLENDS EXHIBITING LOW PERCOLATION THRESHOLD

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Polyaniline (PANI) protonated with camphorsulfonic acid (CSA) was used in the fabrication of conductive polyaniline/poly(methyl metacrylate) (PMMA) blends. Extremely low percolation thresholds were obtained, especially for blends plasticized with dibutyl phthalate (DBP) which reached 0.04 wt % for 35 wt % of DBP content. Conductivity as a function of temperature has been measured from 317 K down to 4.2 K. All prepared blends show a metallic behaviour, however the temperature range of metallic conductivity decreased with decreasing PANI content. At low temperatures the conductivity follows a generalized hopping law. Dynamic Mechanical Analysis (DMA) was performed in the glass-rubber transition temperature range. For PANI content as low as 0.2 wt % significant changes were observed with respect to the pure matrix. A strong increase of the relaxed modulus as well as an alteration of cooperative motions of long chain sequences associated to T_g , displayed through a broadening of the loss angle tangent peak ($\tan \delta$) were reported.

TODAY PARA-ARAMIDE FIBRES ACHIEVEMENTS IN STRUCTURE ORDERING AND PROPERTIES REGULATION.

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INTRODUCTION

There were created the original “family” of industrial produced high-strength, high-modulus fibres and yarns for technical textiles and construction composites based on aromatic para-polyamides - poly-para-phenylene-terephthalamide (Kevlar, Twaron), some like copolymers (Terlon, Technora), poly-para-heteroarylenes (SVM, Armos).

There are publications about every separate para-aramide fibre, but there aren't any comparative analysis of structure and properties peculiarities and, moreover, physical-chemical principles of para-aramide fibres super-molecular structure and properties regulations.

The review and comparative picture for main para-aramide fibres structure and properties, their properties regulation possibilities are presented in this paper and structure optimization ways discussed.

PRINCIPLES OF FIBRE-FORMING

The high-oriented para-aramide fibres formation is based on aromatic linear polymers transformation possibility to liquid-crystalline state. There is spontaneous ordering effect for these fibres in the case of small initial orientation presence. This effect can be both on fibre-forming stage and thermal treatment too. The regulation of structure ordering in initial solution and secondary ordering in solid state by copolymers application is the additional possibility of resulting fibres properties arising. Thermodynamic more advantageous is the state of 3-D order for homo-polymers but this principle go to conflict of kinetic peculiarities by high-ordered fibres structure creation. Therefore was done necessity to synthesize new copolymers with limited molecular rigidity and new suitable fibre-forming methods.

FIBRES STRUCTURE PECULIARITIES

The main peculiarities of structure and energetical structural characteristics for para-aramide fibres are discussed. These indexes include: optimal molecular polarity and rigidity, energy of inter-atomic and inter-molecular interaction, 3-D regularity, axial orientation, equal length of molecular chains in amorphous regions etc. The molecular Structure of para-polyamides is characterized high rigidity and polarity, therefore regular para-aramides can be in liquid crystalline state. Supermolecular structural level is characterized of fibrillar high oriented structure based on straight molecular chains.

It will be noted difference in para-aramides 3-D regularity - presence of asymmetric hetero-cycles prevent from high liquid crystalline ordering in solutions and give 1-D crystallinity order by fibres ordering only.

The aromatic structure, high interatomic and intermolecular bonds energy, high number of stress-holding molecular chains and other peculiarities determine para-aramide fibres high mechanical and thermal properties. The homogenous fibres micro-structure is very important for high mechanical properties too.

Mechanical properties of para-aramide fibres are characterized high modulus (130-160 GPa) strength (range of 3.5 - 5.5 GPa) and small deformativity. Theoretical and limited obtainable mechanical properties analysis and comparison with real achieved indexes show the principal possibility of mechanical properties increasing mainly owing to structure defectiveness elimination.

The peculiarity of para-aramide fibres is high mechanical properties anisotropy (low across indexes), therefore limited strength by pressing and shear, moreover light fibrillation.

Thermal properties of para-aramide fibres are characterized by high glass transition temperatures (270 – 360 centigrades) and high exploitation temperature levels - for PPhTA fibres till 250 - 270 centigrade and for hetero-cyclic para-aramide fibres till 300 – 330 centigrade. Another thermal properties is high inflammability resistance, which is for PPhTA fibres lower (oxygen index 27-30%) than for hetero-cyclic para-aramide fibres (approximately 37 - 43 %).

ARMOS FIBRE PROPERTIES

There were investigated wide complex Armos fibres mechanical and thermal properties in comparison with other para-aramide fibres. Today Armos fibres and yarns have advantages in contrast of other mentioned above fibres in mechanical and thermal characteristics. At present time J.-S. Company "TVERChimvolokno" produce yarns and roving Armos^R with tenacity more than 4,5 - 5.0 GPa, elasticity modulus more than 145 GPa. This yarns are the highest thermo-resistance at exploitation conditions and hard-inflammable.

Application of para-aramide fibres in textiles and composites are determined of high axial mechanical properties in longitudinal loaded manufactured goods. Hybrid materials with carbon or glass fibres are applicable for fibrous materials strengthening by pressing and shear.

CONCLUSION

Comparative analysis of structure, properties and application peculiarities for main kinds para-aramide fibres assist to optimize ways of their development and application. This analysis show further possibility of para-aramide fibres mechanical properties improving by the way of molecular structural rigidity and kinetic of structure building optimization.

SURFACE STRUCTURING OF SYNTHETIC FIBRES BY UV LASER IRRADIATION

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A modern technique for a controlled surface modification of synthetic fibres consists of the irradiation with a pulsed UV laser, which can be used to execute submicrometre surface treatment on polymers.

Many types of synthetic fibres, e.g. poly(ethylene terephthalate PETP), polyamides and aramides, show a characteristic surface modification when irradiated by UV laser. The originally smooth surface of these fibres changes to a rather regular roll-like structure perpendicular to the fibre axis after this treatment.

An investigation of the mechanism of the UV-laser-induced temperature field in the PETP-Polymer is presented. We discuss a specific mathematical solution of the heat equation for large-area (uniform) irradiation on the PETP-substrate in dependence on laser parameters (wavelength, absorbed laser light and laser pulse duration) and substrate parameters (optical absorption coefficient, thermal conductivity and heat diffusivity).

The structuring effect is purely due to the thermal behaviour of surface of the fibre during the laser pulse. The release of frozen-in tensions within the fibres are coupled with high temperature gradients, thus leading to a cooperative movement of polymer chains.

By this surface structuring effect an increase in the wetting properties and adsorption of textile finishing agents are observed. Furthermore, the adhesion of particles, pastes and pigments of synthetic textiles is enhanced.

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MICRO- AND NANO-CELLULOSIC FIBRES – CONDITIONS OF THEIR SPINNING

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The rheological investigations of the cellulosic solutions in the N-methylmorpholine-N-oxide (NMMO) have shown their anisotropic properties. This fact and the acquaintance of the dependence between linear density of the filament and filament tenacity stimulated the expediency of the micro- and nano-cellulosic fibres preparation by the well-known dry-jet wet spinning method of anisotropic solutions of the cellulose. This type of the cellulosic fibres has immense utilization significance considering their high tensile strength, low linear density, excellent hygienic properties, very high moisture transfer and perfect thermal insulation. These fibres can be applied for the manufacture of the high-comfort clothes, clothes to be used in extreme conditions or for manufacture of the special filter stuff, leather like, sound absorbers, medical and other special applications.

FLUORESCENT POLYMER SPECIFICALLY BINDING BIOLOGICAL MOLECULES IN AQUEOUS MEDIA

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Fluorescent indicators are the powerful tools for noninvasive measurements from biological systems. Particularly, the ability to specifically detect biologically active molecules is of primary importance for health care and monitoring. We describe a new approach to fluorescent polymer chemosensor using molecular imprinting technology to construct responsive polymer networks with recognition sites of predetermined specificity. The molecularly imprinted polymer (MIP) serves as both the recognition element and the fluorescent element, intensity of which is dependent on interactions with the guest molecule.

The MIPs are prepared by molecular imprinting [1], which entails copolymerization of functional monomers in the presence of a template (print molecule). Imprinting is achieved by interactions, either noncovalent or covalent which occur between complementary functionalities in the template molecule and functional monomer units. A newly synthesized functional monomer trans-4-[p-(n,n-dimethylamino)styryl]-N-vinylbenzylpyridinium chloride combines microenvironmental sensitive fluorescence, due to its intramolecular charge-transfer behaviour [2], and positive charge that is capable of promoting an association with negatively charged nucleotide ion. Molecular imprints were prepared against cAMP (adenosine 3',5'-cyclic monophosphate) [3]. The functional, fluorescent monomer was polymerized in the presence of cAMP salt and other functional and cross-linking monomers to create a fluorescent molecularly imprinted methacrylate polymer. The solid polymer was grounded to particles of 45-106 μm then the template molecules (cAMP) were removed.

Such fluorescent polymers, capable of specifically detect the cAMP in aqueous media, were examined by steady state and time-resolved fluorescence spectroscopy. The association constant for the binding of cAMP to the imprinted polymer was determined by fluorescence spectroscopy to be in the order of 10^5 M^{-1} in comparizon with relatively low association constant between the fluorescent monomer molecule and cAMP in aqueous solution 14 M^{-1} . The results suggest that the three-dimentional network of the polymer enabled recognition of the size and shape of the model molecule (template molecule).

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MULTIFUNCTIONAL MACROMOLECULES AND STRUCTURES AS ONE-WAY EXCITON CONDUCTORS

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Results of design, first steps in synthesis and possible application of multifunctional macromolecules which possess one-way direct exciton conductivity are presented. Some problems appeared on the way of these systems' creation are examined.

INTRODUCTION

The design and synthesis of functional macromolecules for the information processing, transfer and storage in molecular scale are among the main problems of nanoelectronics. On the other hand, for purposes of chemical engineering the necessity of electronic excitation energy supply (pumping) to the determine points of system or, contrary, its "sucking off" from reaction centers are required.

In present paper the results of authors' works on creation and studying of one-way exciton-conducting macromolecules were briefly reviewed and discussed.

I. MAIN IDEAS AND MODELS

It is known that a motion of singlet (S) and triplet (T) excitons along homopolymer macromolecule is one-dimensional random walks in a character [1]. The direct (one-way) exciton current in macromolecule is possible only if the determine hierarchy of macromolecular cells' energy levels takes place.

Two macromolecular models with direct current of excitons have been proposed.

A) Proposed model [2,3] is the macromolecule which consists of practically independent π -electron systems. The position of the first singlet excited level of the initial π -electron system of macromolecule is lower then for the other cells in the macromolecule but gradually lowering of triplet levels takes places along the chain. In this case the selective exciting of the first cell of macromolecule leads to the direct one-way triplet propagation

from initial to end cell along the macromolecule. The value of triplet exciton current through link number n

$I_n = I_0 [(1-\alpha)/(1+e^{-\Delta E/kT})]^n$ (where α - the average possibility of spontaneous deactivation in every elementary unit of macromolecule, ΔE - energy difference between triplet levels of neighboring units).

B) The another model proposed [4] is nonlinear branched macromolecule, each branch of which has the same energy structure as in model described above. Such macromolecule model could give the possibility to create the excited sites with high density population in end common cell.

The first steps in synthesis of these models have been made [3,5].

II. PROBLEMS IN DESIGN AND SYNTHESIS

1. Problem of the first macromolecular cell selection.

The initial value of T-exciton current (I_0) mainly depends on $S_1 \rightarrow T_1$ transition's probability in the initial elementary cell of macromolecule. That's why the initial link must include π -electron system with essential probability of $S_1 \rightarrow T_1$ transition. The benzophenone-type system may be used with this aim. However, as we founded [6], there is another solving of this problem. We have shown that there is a possibility to select such two π -electron systems that one of them induces the increasing of $S_1 \rightarrow T_1$ transition's probability in another.

2. Dependence of singlet-triplet splitting on macromolecular chromophore structure.

Up to now this problem has being solved mainly empirically. However, the principal solution is necessary. Some approaches for solving this problem are proposed.

3. Difficulties in synthesis.

The practical creation of such macromolecule is a very difficult task. Every link of this macromolecule must be different, with new position of singlet and triplet energy levels. To our point of view, the photochemical methods are perspective for solving of this problem. Some new proposals in creation of such systems are examined.

III. APPLIED PROBLEMS

To our opinion, macromolecules of type A and B can be used as basic elements of molecular electronics (exciton rectifiers, or one-way exciton conductors for example). Macromolecules of B-type can be also used for polymer laser creation.

On the other hand it can be applied in chemical engineering and photochemistry for pumping (or contrary "sucking off") the energy to reaction zones of media. This possibility has been checked by us for acceleration or stopping of such photochemical reaction as Fries photorearrangement [7].

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MOLYBDENUM DISULFIDE INTERCALATES WITH SPECIAL TRANSPORT PROPERTIES

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Molybdenum disulfide like many other layered transition metal chalcogenides undergoes quasi-topotactic reactions intercalating chemical species in two-dimensional interlaminar spaces. Intercalation products displaying a wide range of stoichiometries are potentially useful as materials with tunable properties. The aim of the paper will be to review relevant aspects of the MoS₂ intercalation chemistry – synthesis and characterization of the products, structure-properties relationships, thermodynamics and kinetics of the intercalation reaction, and transport properties, specially those related with the mobility of ionic species in the interlaminar spaces – highlighting those aspects related with the application of these compounds as materials for electrochemical devices.

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ORIGINAL IMPULSE-ACOUSTIC METHOD FOR FIBRES BUNDLE (YARN) INNER DEFECTIVENESS AND DESTRUCTION TESTING. PRINCIPLES AND DEVELOPMENT

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INTRODUCTION

The inner defectiveness and unevenness of yarns and other textile structures are the important information of their quality and reliability in processing and exploitation. We suggested and elaborated new impulse-acoustic method, which give original information about defectiveness rate of every included structural elements (fibres or filaments) of yarn or other fibrous structures. There aren't publications about application of this method to bundle of fibres, yarns and other fibrous materials especially reinforcing yarns and rovings for inner defectiveness and unevenness determination.

Our investigations of impulse-acoustic method began some years ago. The main principles and development results are presented in this paper.

PRINCIPLES OF METHOD

This method based on determination of impulse-acoustic signals by loading of multi-elements materials (fibres bundles, yarns, threads, textiles etc.) to every structural elements (fibres) rupture. Deformation energy of every element get free by rupture and give return impulse. These impulse, their intensity, arrangement etc. are registrated and give the impulse-acoustic spectrum-picture during material step by step destruction. At the same time are registrated the traditional mechanical characteristics, for example full diagram load-deformation (including right part).

It will be noted the principal differences this method in comparison to continuos solids application. The solids are characterized of cracks propagation and therefore interpretation of tests results is indefinite.

EXPERIMENTAL METHOD, PROCEDURE AND RESULTS

The fibres bundle (or yarn) is loaded and stretched to full rupture. The break of every filament during stretching gave separate acoustic impulses which are registered by impulse-acoustic sensor.

The series of our investigations concerned of impulse-acoustic method application to high-strength reinforcing fibrous structures. The main objects were high-strength aliphatic polyamide, hydratcellulose yarn (tyre-cord) and para-aramide super high strength yarns.

The best information in results interpretation is obtained by combination of impulse-acoustic spectrum with full deformation diagramme to rupture. The impulse-acoustic spectrum and full stress - strain diagram both permit to find of every impulse coordinates. These data show an excellent picture of destruction process graduation (distribution during time or deformation).

POSSIBILITY OF IMPULSE-ACOUSTIC METHOD

There are a wide variety of impulse-acoustic spectrum for different multi-filament yarns, which differ of acoustic impulses arrangement. The impulse-acoustic spectrum scanning permit to understand fibrous structure rupture mechanizm and therefore defected fibres or filaments arrangement. Only one compact group of rupture impulses is characterizing uniform bundle (yarn) without defects. The more are ununiformity and defectiveness of fibres bundle (yarn), the more width of impulse group position. The magnitude and position of first impulse or first impulses small group and distance from main rupture impulses group give information on "week place" and their amount (defected structural elements - filaments). These information can't displayed by other methods.

CONCLUSION

The principles, possibilities and investigations results for many different fibrous materials are presented in this paper. Impulse-acoustic emission method maybe very interesting for diagnostic of rupture mechanism and defectiveness of different fibrous materials, including yarns, threads, bands, woven structures.

This method possible to applied both to destructive researches and to listening of friction moving of fibres in fibrous structures.

UV-BEAM POLYMERIZABLE NANOPARTICLES AS SCRATCH RESISTANT COATINGS

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A photochemically curable transparent hard coating material has been developed to improve the wear resistance of organic polymers. Methacrylate functionalized silanes and nanoscaled boehmite particles have been used for the preparation of the UV curable hard coatings by the sol-gel technique. The inorganic network is formed as a result of the controlled hydrolysis and condensation of the methacryloxysilanes in the presence of nanoparticles (particle size: 15 nm). The hydrolysis and condensation of the methacryloxy silane for two hours in presence of boehmite nanoparticles (43 wt.%) at 100 °C leads to a degree of condensation of 80 % of the inorganic network as determined by ^{29}Si -NMR spectroscopy. The formation of the organic network results from subsequent UV induced polymerization of the methacrylic groupings by using a UV photoinitiator and determined by IR-spectroscopie. The polymerization process requires several minutes only by UV light of a Hg high pressure lamp. In order to increase the flexibility multifunctional methacrylate monomers and polyester- or urethanacrylate oligomers are copolymerized in concentrations up to 20 mole-%. Transparent coatings on plastic substrates (PC, PMMA) have been produced by spray or spin coating with good optical quality and thicknesses of several micrometers. The transparent coatings show excellent adhesion onto PMMA and PC (CC/TT=0/0, DIN 53151) even without using primers and good abrasion resistance after the taber abraser test with haze values of 7-9 % after 1000 cycles (CS 10F rolls, 5,4 N). The water exposition test (65 °C, deionized water) and the Suntest without using filters did not result in any crack formation, loss of adhesion or yellowing within the employed test period of two weeks.

**Polymeric Materials
and Composites
for Electronics
and Photonics**

Invited lecture

MOLECULAR CRYSTALS WITH NONLINEAR OPTICAL PROPERTIES

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In the past decades a great effort has been made in developing of organic materials for the second-harmonic generation (SHG).

It has been demonstrated that organic materials displaying second-order nonlinear optical response are generally built-up with molecules containing a π -conjugated pathway, substituted by an electron – acceptor group at one end and by an electron – donor group at the other end (1). The relevance of such conjugated molecules has been widely emphasized with paranitroaniline derivatives as the prototype family (2).

However to achieve efficient nonlinear optical devices, both high hyperpolarizability and an appropriate noncentrosymmetric crystal structure is needed (1).

Recently it has been shown that some acid-base hydrogen- bonded complexes in solids generate the second harmonic frequency too (3, 4). These complexes will be demonstrated and discussed.

ACKNOWLEDGEMENT

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Invited lecture

NONLINEAR OPTICAL PROPERTIES OF BENZYLIC AMIDE [2]CATENANES :A NOVEL VERSATILE PHOTONIC MATERIAL

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Catenanes are a new class of molecules composed of interlocked rings which may circumrotate one through the other¹. Large catenanes ($M_w=10^5$) are present in nature in DNA as intermediates during the replication, transcription, and recombination process. Since the first two-ring catenane was obtained in 1960^{1a}, smaller synthetic catenanes ($M_w=10^3$) have attracted the interest of chemists. Although they were once considered as exotic chemical species, recently they have been addressed as key elements in the development of components for nanoscale devices (such as molecular switches and shuttles) and information storage systems²⁻⁴. In this respect catenane architectures are particularly attractive because the components of the molecule are held together by a dynamic mechanical bond which can be controlled through local environment and external electric fields. In this paper we will report on linear and nonlinear optical properties of this molecules in thin films and in solution. Benzylic amide [2]catenanes can be processed into good optical propagation properties thin films with large, as for organic materials, index of refraction. They show interesting third order properties as evidenced experimentally by the optical third harmonic generation techniques and by the electro-optic Kerr effect as well as by quantum mechanical calculations. As grown thin films exhibit also second order NLO properties evidenced by the optical second harmonic generation and by modulation ellipsometry.

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Invited lecture

ABSORPTION CONTROL OF AN EO-POLYMER AND A SHG-CRYSTAL FOR DEVICE APPLICATIONS

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Organic NLO materials with a large optical nonlinearity, with fabrication technology for device structure, and with low absorption loss at wavelengths to be used, can be applied as actual photonic devices. To attain these required features, we have focused on the reduction of absorptional loss of an EO-polymer, i.e., an azo-dye-attached polymer, and an organic crystal, i.e., 2-adamanthylamino-5-nitro pyridine, AANP for short. By using monodispersed polymer as a matrix for an azo-dye, absorptional tail of the dye attached polymer is effectively reduced at a visible wavelength region. For AANP crystal, reduction of absorptional loss at 1.55 μm is effectively attained by converting hydrogen to deuterium which combines with amino group of the molecular structure. These results allow us to use these organic NLO materials such actual devices as optical information process and optical sampling systems.

Invited lecture

NOVEL PHOTONICS POLYMERS IN HIGH-SPEED TELECOMMUNICATION

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Recent status of the polymer optical fiber (POF) for high-speed telecommunication is reviewed. The GI POF was proposed from Keio University in 1982 for the first time and several methodologies to fabricate GI POF have been currently proposed worldwide. In this paper, we propose the promising GI POF which has both lowest transmission loss and highest bandwidth based on the material characteristics such as scattering, material dispersion, etc.

Regarding the bandwidth characteristics of the GI POF, we have proposed the ideal refractive index profile of the CI POF which enabled to transmit the order of giga bit per second for more than 100 m length. There are several reports of the theoretical bandwidth estimation of the GI POF, and generally the expected bandwidth characteristics are different from the measured one. In those reports, the main reason of disagreement of calculated and measured bandwidth characteristics has been explained by the mode coupling. However, it is clarified in this paper that the effect of the mode coupling on the bandwidth characteristics of the GI POF is weak for about 100 m length, and the differential mode attenuation strongly affects the bandwidth characteristics of the GI POF by investigating lots of CI POFs having different index profiles.

We have also proposed an HSOT polymer for use as a high luminance light medium. This polymer contains specified internal microscopic heterogeneous structures for controlling light scattering properties. An LCD backlight using the HSOT polymer has twice the brightness of the conventional transparent PMMA-based backlight because of multiple scattering phenomenon inside the HSOT polymer. In this paper, such a light scattering phenomenon was quantitatively analyzed by a ray tracing based on Mie scattering and Monte Carlo simulations. Subsequently, we proposed the new HSOT backlight system having higher luminance and uniformity of white color illumination.

*Invited lecture***THIRD-ORDER NONLINEAR OPTICAL EFFECTS DUE TO ONE AND TWO-PHOTON ABSORPTION IN CONJUGATED POLYMERS****M. Samoć, A. Samoć and B. Luther-Davies**

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We investigated third-order nonlinear optical effects in several π -conjugated polymers, including well-known materials such as poly(*p*-phenylenevinylenes) (PPVs) with different substituents, polyanilines, and less known structures such as polyindeno[1,2-b]fluorene (PIF). Several experimental techniques have been employed to obtain information on the magnitudes of the real and imaginary parts of the third-order nonlinearities of these polymers, the most convenient techniques being Z-scan (especially when performed on solutions of the soluble polymers) and time-resolved degenerate four-wave mixing (DFWM) with detection of phase-matched and non phase-matched signals [1]. Relatively large values of the nonlinear refractive index n_2 could be obtained in some cases, up to five orders of magnitude higher than the nonlinearity of silica glass. The major problem with such materials is, however, that linear (one-photon) and nonlinear (two-photon) absorption is often excessive for waveguiding applications.

We investigated the nonlinear phenomena involved in the femtosecond response of various polymers. In the case of poly(phenylenevinylenes) we found that two-photon induced excited species are generally responsible for varying relaxation times of the complex susceptibility change induced by a short laser pulse (see e.g. [2]). In polyanilines and PIF, however, the main effect is derived from one-photon produced excitations and absorption saturation becomes a dominant factor. Saturation effects may lead to very high effective nonlinearities [3] and are, therefore of interest from device application point of view. We find that the relaxation of the NLO effect in PIF is relatively fast ($T_1 \approx 2$ ps) and our measurements indicate that the coherence time T_2 may be relatively long: on the order of 200 fs.

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Invited lecture

ORGANIC MATERIALS RESEARCH FOR AEROSPACE OPTOELECTRONIC APPLICATIONS

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The use of high performance organic and polymeric materials in advanced aerospace applications is well established and increasing applications requirements are generating research leading to new materials with enhanced performance capabilities. Continuing advances in organic materials technology are also creating new possibilities for novel materials usage in aerospace applications. This presentation will give an overview of two examples of organic and polymeric materials research currently underway in the Materials and Manufacturing Directorate of the Air Force Research Laboratory: (1) organic chromophores with increased two-photon activity; (2) electrically conducting high strength organic fibers.

Although the concept of two-photon absorption (TPA) has been extensively investigated, the utilization of this phenomenon for practical applications has been impractical because of the inadequate activity of currently available chromophores at the requisite wavelengths. New highly stable and soluble organic chromophores have recently been synthesized via innovative multi-step organic sequences and molecularly tailored in order that two-photon absorption would fall at 800 nm, a region of high transparency for most organic materials. The design, synthesis, and characterization of these new chromophores is part of a collaborative effort with the Photonics Research Laboratory at the State University of New York at Buffalo and has opened up new applications areas which combine TPA with the phenomenon of upconverted fluorescence emission to address difficult aerospace materials problems. Of particular current interest is the use of these related phenomena for three-dimensional fluorescence imaging for corrosion detection on aircraft surfaces.

In response to the critical need for new light-weight, high-performance, electrically conductive polymeric materials for aerospace applications, recent research into the hierarchical control of nanoparticle deposition in polymers has been directed toward the development of high-strength, electrically conductive nanocomposite fibers containing an interpenetrating network of metal and polymer. Wet-spinning of lyotropic liquid crystalline solutions of rigid-rod polymers such as poly(p-phenylenebenzobisthiazole) and poly(p-phenylenebenzobisoxazole) with concurrent in-situ deposition of silver led to high performance electrically conductive nanocomposite fibers with conductivities exceeding 10^4 S/cm. These environmentally stable fibers exhibited excellent mechanical properties

similar to those of the parent polymers. It is expected that the lightweight nature of the fibers will impact both space and aerospace vehicles and that the high strength and modulus will lead to enhanced durability in applications such as signal cables in aircraft and satellites.

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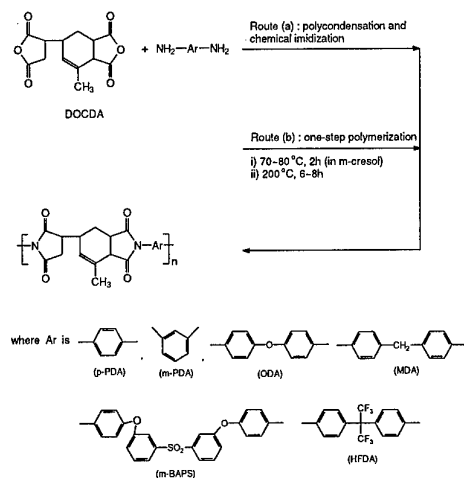
*Invited lecture***SYNTHESIS AND CHARACTERIZATION OF COLORLESS POLYIMIDES FOR LIQUID CRYSTAL ALIGNMENT LAYER****Kil-Yeong Choi, Mi Hie Yi**Advanced Materials Division, Korea Research Institute of Chemical Technology
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Aromatic polyimides have been widely used as the materials for the electro-optic devices owing to their excellent characteristics such as good thermal property, mechanical property and electrical property, etc. However, most of polyimides are insoluble-infusible and high cost, which limits their wide applications. Therefore, significant synthetic efforts have been conducted to improve the processability and solubility of polyimides with the retention of their attractive properties by the introduction of new structures into polymer backbone. Especially, it is well known that the incorporation of asymmetric alicyclic structure into polymer backbone increased solubility and processability, remarkably. However, there were no systematic studies on the synthesis and characterization of alicyclic polyimides with asymmetric structure. Therefore, we have undertaken research on the synthesis of the novel polyimides from alicyclic dianhydride, 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (DOCDA) and various aromatic diamines. And we have studied on the structural changes of polymers with different reaction conditions. All of the polyimides were synthesized by one-step polymerization in *m*-cresol as well as the chemical imidization method as shown in scheme 1. The prepared polymers were soluble in common organic aprotic polar solvents and gave the tough and flexible films. The dielectric constant and birefringence of the resulting polymers were measured to inquire the electro-optic properties.

The thermal properties and the transparency of the polymers were determined by DSC/TGA and UV-Vis spectroscopy, respectively, which was enough for the application of liquid crystal alignment layer.

Therefore, in this study, we have also prepared a class of the soluble polyimide based on the above dianhydride (DOCDA) and the specially designed aromatic diamine with long alkyl side chain, which can be used for liquid crystal alignment layer. The relationship of the polymer structures and the properties such as the pretilt-angle, liquid crystal alignment property and surface morphology was investigated in detail. The glass transition temperatures of the obtained polyimides were decreased with the increase of the alkyl side chain composition. The resulting polymers were highly soluble in aprotic polar solvents such as NMP, DMSO, DMF, and DMAc, etc, which was improved with the increase of the content of alkyl side chain. Furthermore, these polymers gave excellent liquid crystal

alignment properties as well as high pretilt angles, which was increased by the incorporation of the long alkyl side chains and ranged from 1.99 to 7.00°.



Scheme 1

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Invited lecture

ORIENTATIONAL PHOTOREFRACTIVE EFFECT OF NEMATIC LIQUID CRYSTAL/ C_{60} MIXTURE BETWEEN PVK LAYERS

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For the last couple of years photorefractive composites containing liquid crystals have emerged as a promising recording medium for holographic optical devices. The nematic phase, one of the various liquid crystal mesophases, is known to have large Kerr-like optical nonlinearities associated with the director axis reorientation by an optically induced field. Also, nematic liquid crystals have a directional order despite their low viscosity, which allows for a greater orientational displacement for a given space-charge field. This space-charge field is caused by the non-uniform illumination of two-mutually coherent writing beams. The hologram is stored in the form of a refractive index pattern resulted from the orientational birefringence modulation of liquid crystal induced by the space-charge field. In this study, we reported the photorefractive effect from E7- C_{60} -PVK(poly(N-vinylcabazole)) mixture in several different geometry. The effects of position and concentration of C_{60} to the two-beam coupling gain were checked.

Invited lecture

**MOLECULAR ORGANIC LIGHT-EMITTING DIODES BASED
ON A GUEST-HOST ACTIVE LAYER**

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High electroluminescence (EL) quantum efficiency and thermal stability have been achieved in molecular organic light emitting diodes based on a guest-host active layer. This layer consists of highly fluorescent guest molecules dispersed in an organic host matrix with dual luminescent and carrier transporting properties. EL quantum and power luminous efficiencies are found to be independent of temperature up to the glass transition temperature of the hole transport/injection material employed in the device. The talk addresses the role that the guest molecule plays in improving the device efficiency and lifetime including the various possible EL mechanisms. Efficient Fvrster energy transfer from host to guest molecules and/or direct carrier recombination at the highly fluorescent guest molecules are discussed in this context.

*Invited lecture***NEW DESIGNS FOR POLYMER LEDS****Frank E. Karasz**Department of Polymer Science & Engineering
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Multilayer architectures provide enhanced efficiencies in polymer LEDs principally by virtue of their ability to provide a more balanced charge injection and good excitonic confinement within the chromophore layer. Further improvement may be gained by using the same charge transport materials in a multi-component design which relies on the immiscibility of the respective polymeric constituents to provide micro-domains (“quantum wells”) of the chromophore in a matrix of the other components. Using alternating hard-soft block copolymers in which the oligomeric hard block forms the chromophore while the soft block provides solubility and an additional discrete phase, we have designed systems which emit blue, green or red, as required, from a single layer device. Further advantages of the multicomponent design include more versatility in optimizing charge injection by adjusting the ratio of the electron and hole transporting materials, and reduced concentration quenching in the chromophore because of its dispersed state. By using a chromophores blend, one may also take advantage of energy transfer from the higher to the lower band gap material. Fabrication of a single layer device is simplified in comparison to a multi-layer architecture.

The multi-component design has been developed to produce a white light emitting polymer LED. The chromophore domain is a blend of the blue, green and red emitters in appropriate ratio, while the charge transport components optimized by the usual criterion of balanced injection from the matrix. Because of the differing band gaps and ionization potentials of the chromophore components the emission spectrum is field dependent; a CIE chromaticity diagram analysis showed a shift in the spectrum as the bias voltage was increased, progressing from orange-red to white as the green and blue chromophores became activated.

*Invited lecture***ELECTROLUMINESCENCE IN MOLECULARLY-DOPED POLYMERS****J. Kalinowski**Department of Molecular Physics, Technical University of Gdańsk,
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Electroluminescence (EL) defined as a direct transformation of electrical energy into light involves excitation of electronic states by a voltage applied to a luminescent substance. Among various modes of their excitation the recombination of electrons and holes injected from electrode contacts into thin organic films has recently drawn the wide-world attention due to a great deal of their potential use for displays [1]. EL devices based on molecularly-doped polymers (MDPs) are of particular interest because of certain advantages over evaporated dye films and those fabricated with intrinsically conductive polymers. MDPs show the distinctive ability to select an emitter molecule that fluoresces in a desirable spectral range and possibility to tune the transport properties by proper selection of dopant molecules and their concentration in inert, electronically inactive polymeric matrices. Selecting the host polymer matrix and single layer (SL) structure of EL devices allows one to optimize the mechanical properties of MDPs and simplifies their fabrication by enabling spin coating techniques to be used. To improve the performance parameters of MDP-based EL devices requires knowledge concerning the mechanism by which charge carriers are generated, transported and combined. Like other organic recombination EL devices, the function of the MDP-based light-emitting-diodes (LEDs) is governed by the relation between the transit (τ_t) and recombination (τ_{rec}) time of the charge carriers injected from electrodes into organic components of the LEDs [2]. These are determined by charge injection ability of electrode-polymer interfaces and transport properties of MDPs. The relation between τ_{rec} and τ_t has been used to distinguish two limiting cases of the recombination EL mechanism: (i) Injection-Controlled EL (ICEL) ($\tau_{rec} > \tau_t$) and (ii) Volume-Controlled EL (VCEL) ($\tau_{rec} < \tau_t$) [2]. The EL efficiency, defined as

$$\varphi_{EL} = \frac{\varphi_{PL} P_1}{1 + \tau_{rec} / \tau_t} \quad (1)$$

is of the essential importance in LEDs converting current to light (here φ_{PL} is the photoluminescence efficiency and P_1 is the probability of a recombining electron-hole pair to yield an emitting singlet excited state).

This paper presents analytic considerations relating EL output to carrier injection and transport mechanisms completed with electron-hole recombination process in SL as well as double-layer (DL) MDP-based EL devices featuring interfacial charge accumulation. The

paper is divided into two sections. The first one delineates the importance of the field-dependent mobility as a condition for the EL yield to be independent of the driving current in the SL MDP-based EL structures operating under ICEL mode. The effect of the hole transport material and electron transport material concentration on electrical and optical characteristics of such EL devices is examined using as an example an ITO/Polycarbonate (PC)+Aromatic diamine (TPD)+Alq₃/Mg/Ag SL LED fabricated by a spin-coating technique. As predicted by the discussed theoretical model, the EL efficiency appears to be independent of the driving current which is manifested by the quasi-linear brightness-current relationship. The EL yield and its relation to the driving current appears to be only slightly affected by the concentration ratio TPD:Alq₃. Its increase lowers the EL yield but strongly raises the absolute EL output. The conditions are examined to fabricate the MDP-based LEDs for different applications: for these where power consumption is of priority importance (high efficiency LEDs) and those where the high brightness of the EL display is required (high brightness LEDs). In the second part the EL efficiency is related to the driving current in conjunction with varying concentration of hole transporting molecules in the hole transport layers of DL EL structures composed of an MDP hole transport layer (HTL) and a vacuum-evaporated onto it low-molecular weight material electron transport layer (ETL) acting as an emitter (EML) too. The experimental data obtained with ITO/(PC+TPD)/Alq₃/Mg/Ag DL LEDs show the ϕ_{EL} maxima at electric fields $F_c > 10^6 \text{ V/cm}$ dependent on the PC:TPD concentration ratio and thickness of the electron blocking layer. The results are discussed in terms of charge recombination at the internal HTL/ETL(EML) interface including an enhancement of the anodic side field giving rise to enhanced hole injection. However, an electric field effect on recombination rate had to be invoked to explain a field decrease of ϕ_{EL} above F_c . A comparison of operation mechanisms of MDP-based LEDs with other organic EL devices has shown some important differences allowing to improve understanding the LED operation mechanism in general and to undertake proper steps in preparation of desirable performance parameters organic LEDs.

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Invited lecture

USABILITY IN THE LED'S DEVICES OF POLYMERS MODIFIED BY CHANGING THE CARBAZOLE GROUP

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The story of the light emission diode's made of polymer started in 1980 with the report by a Cambridge group, which dealt with the light emission occurring when the voltage was applied to a thin film of the PPV polymer. Today, polymer LED's studies are conducted by a lot of scientific groups in the world. They use a great many methods to receive diodes emitting different colors with better efficiencies and a longer lifetime. The progress made regarding the properties has required betterment of interdisciplinary approach in which chemists and physicists work closely together.

Our group chose five methods of approach to the LED structures:

1. Changing of substituents in the carbazole group by inserting Cl, Br, I in position 3 or 3 and 6 in poly(N-vinylcarbazole) (PVK)
2. Blends of PVK with poly(alkylthiophene)
3. Co-polymers of 2-(9-carbazolyl) ethyl methacrylate (CEM) and 3-phenyl-7-methacryloyloxyethoxy-1-methyl-1H-pyrazolo[3,4-b]quinoline.
4. Polyalkilocarbazole
5. Polycarbazole

There are many advantages of polymer LED's as far as the displays are concerned. The displays emit different color light giving excellent contrast and viewing angle.

A simple polymer LED is made by spin-coating the light-emitting polymer layer onto a contact (ITO) followed by evaporation of a top metal electrode. Then a voltage is applied, electrons are injected from one electrode and holes from the other into the polymer layer. The electrons and holes migrate across the polymer layer and can meet up to form an excited state which can decay by giving out light. In most organic materials the injection and transport of the holes is much more efficient than of the electron. This imbalance can give poor device efficiency because many holes will pass through the device without meeting an electron and hence, without emitting light. The region where electrons and holes meet is very close to the metal contact which tends to quench luminescence. Therefore we use calcium as an electron-injecting contact. An alternative approach to improve the electron injection into the polymer layer is to substitute the polymer with electron-withdrawing groups to increase its electron affinity. Another very successful approach is to make LEDs consisting of two or more polymer layers.

The polymers for LED's must be processible, emit light of a suitable color, transport charge and be thermostable and photostable. Different colors can be obtained by changing the polymer.

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Invited lecture

OPTICALLY ADDRESSED LIQUID CRYSTALLINE LIGHT VALVES – THEORY OF THEIR OPERATION AND APPLICATIONS

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Reversible laser induced dynamic refractive index gratings or holograms produced in liquid crystals were reported by several groups [1-4]. Among various processes leading to creation of index grating in liquid crystal those connected with molecular reorientation due to light driven internal electric field modulation are of primary importance. This can be done by intrinsic photoconductivity of the liquid crystal mixture or by use of semi-transparent photoconducting electrodes. Our research was focused on developing optically addressed light valves, their characterisation, performances and drawbacks. Depending on construction of liquid crystal panels, materials used or even external optical systems several useful optical devices has been constructed, like: phase conjugating mirror, Fourier optical correlator for pattern recognition, coherent light amplifier, incoherent-to-coherent light converter, etc. The understanding of principle of operation of each photoactive element deserved the physical description involving the electrical transport properties of liquid crystal used (ion mobilities, photoconductivity, role of dyes and also resistivity of electrode materials, etc.), its optical properties (birefringence, order parameter, light scattering, dynamics of molecular reorientation and index profile along the thickness). These problems will be addressed in the present communication. We also show some recent experimental results obtained with various nematic liquid crystal systems promising for their application in optical computing, interconnection, optical image processing and storage.

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Invited lecture

**CHARACTERIZATION AND APPLICATIONS
OF CROSSLINKABLE MATERIALS**

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Crosslinkable photosensitive materials have been studied for many years and they are widely used optical recording of information. After investigating the photochemical process in various systems, it appears that the chemical structure of the polymeric matrix plays an essential role in the process of the reaction that takes place upon irradiation by a laser beam. We also investigated the possible use of different sensitizers and different mixture of polymers. We will discuss some applications that were studied using such crosslinkable systems. We will show that they can be used as volume holograms as well as surface relief systems.

Invited lecture

PHOTOCHROMISM AND PHOTOASSISTED POLING IN POLYIMIDES

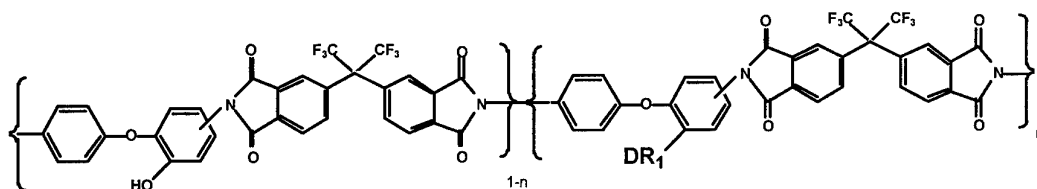
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We synthesized and characterized side-chain polyimides bearing Disperse Red One groups (PI-co-DR1)¹. These copolymers are soluble in organic solvents in spite of their fully imidized structure, which allows the preparation of thin films by spin coating, and they have a very high glass transition temperature ($T_g \geq 250^\circ\text{C}$), which has been shown to be efficient to achieve stable second order non linear optical coefficients in poled polymers for second order nonlinear optics (second order NLO).¹ The structure of this copolymer is shown below:



One of the drawback of using these high T_g polymers is the use of high poling temperatures T_p ($T_p \approx T_g$), which lead to some irreversible chemical degradation of NLO chromophores, particularly DR1.² In order to prevent such a chemical degradation, we proposed to use photoassisted poling (PAP) and we demonstrated that it was an efficient way to orient DR1 dipoles in PI-co-DR1 at room temperature or at temperatures far below T_g .²

We present here different results concerning photochromism and time-resolved photoassisted poling of DR1 during SHG measurements with in-situ poling. First, quantum yields of photoisomerization of E-DR1 to Z-DR1 (Φ_{E-Z}) and of Z-DR1 to E-DR1 (Φ_{Z-E}), together with the thermal back isomerisation rate constant have been determined and compared with the values in PMMA, a much less rigid matrix. Secondly, the dynamics of PAP at different temperatures has been studied and shows the efficiency of the method. Degradation ratios of DR1 have been determined together with orientation factors at different poling temperatures. The use of both polarized light and heat proved to be an efficient method to prepare poled samples. One drawback of PAP is a decrease in thermal stability of the poled films compared with those poled thermally. However, we have shown

here that the stability of the poled samples is dependant upon the temperature of the PAP : the higher this temperature, and the higher the disorientation temperature. A secondary glass transition temperature around 130°C plays an important role in the dynamics of these disorientation processes in polyimides.

Finally, the influence of polarized light on an initially oriented sample of PI-co-DR1 has been studied by SHG : it leads to an irreversible loss of SHG property, as a consequence of a complete disorientation of chromophores under irradiation. This is different from the observed modulation of the $\chi^{(3)}$ coefficient by irradiation with polarized light under an external electric field, which does not need to preserve non centrosymmetry.³

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Invited lecture**SILICA-BASED GLASSES AS PHOTONIC MATERIALS****Akira J. Ikushima & Takumi Fujiwara**Advanced Photon Technology Center, Toyota Technological Institute
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Glasses are the material with the inversion symmetry, and therefore it cannot have any even-order optical nonlinearities and cannot be used in principle for active devices. After a pioneer work by Fujiwara et al. [1], research group of the present authors has revealed that, with a special treatment to break the inversion symmetry, an appreciable second-order optical nonlinearity is induced in Ge-doped silica glasses. The treatment, so-called the UV-poling, is simultaneous applications of a high enough d.c. voltage and UV-light irradiation.

Table I shows values of the second harmonic generation coefficient, d , thus induced in bulk 15 mole% Ge-doped silica glass, together with those in some typical crystals. The value has already exceeded d_{13} of LiNbO₃. Moreover, the value could be increased after a heat treatment in vacuum and at high temperatures, which is the fact to indicate that the second-order nonlinearity is relevant to oxygen-deficit defects in silica glass. Comparing with crystals, splendid optical transparency, wider wavelength range of the transparency, much better fitting to fiber network and other more advantages with glass materials are superb.

Probably decay of the effect as time passes should be more serious besides the magnitude of d -coefficient. The decay time has been found to be closely related, at least in bulk glasses, to the dark conductivity in UV-poled silica [2]. This means that charge carriers move back in some way to reduce and degrade the induced nonlinearity. The present authors are now trying to identify the carriers and reduce the mobility.

Recent progress on the induced nonlinearity in Ge-doped silica films will be discussed, and more about various promising applications including film waveguides will be presented at the conference.

Table 1 Comparison of d -coefficient

	UV-poled Ge:SiO ₂ glass	LiNbO ₃	KDP	quartz
d -coefficient (pm/V)	3.4±0.2 (untreated) 5.1±0.2 (pre-heated)	31.0 (d_{33}) 4.7(d_{13}) 3.0 (d_{22})	0.8	0.5

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Invited lecture

POLYMERS FOR OPTOELECTRONIC APPLICATIONS

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The tailoring of organic molecules and polymers has enabled the recent development of multifunctional materials such as photorefractive polymers and organic electroluminescent materials. This talk will review our recent advances in these areas. Topics to be presented on the photorefractive polymers will include: (1) Near IR operation: Photorefractive polymers with an unprecedented performance levels at 830 nm in the near infra-red region of the electromagnetic spectrum and in the visible have been developed by using a new sensitizer and a dye designed to have a high dipole moment and a high linear polarizability anisotropy. (2) Speed enhancement: The response time of photorefractive polymers have been improved by almost three orders of magnitude to 1.8 ms which make them compatible with video rates. (3) Lifetime enhancement: New composites with high efficiency and a long shelf lifetime of several years have been made. (4) Photorefractive PDLCS: The photorefractive effect has been demonstrated in flinctionalized polymer-dispersed liquid crystals. (5) Dynamic range enhancement: In 105 mm-thick samples, overmodulation of the diffraction efficiency was observed for an applied field of 8V/um. (6) Security and biomedical applications: We have used the best photorefractive polymers in device geometry and have identified several niche applications. An all-optical, all-polymeric correlator for security applications was demonstrated. We also initiated a new biomedical imaging technique based on time-gating techniques in a photorefractive polymer.

In the areas of polymer LEDs and Lasers, we report on organic electroluminescent devices based on Al cathode with luminous efficiency of 20 lm/W and external quantum efficiency of 4.6%. when pulsed in air at room temperature and without any encapsulation, high peak brightness of 4.4×10^6 cd/m² and high efficiency of 4.4 cd/A are obtained. We demonstrate that device quantum efficiency can be increased by tuning the ionization potential of the hole-transport moieties. The high efficiency and peak brightness with Al cathode are encouraging for the manufacturing of stable devices and the development of electrically injected organic lasers.

We also present new ways of fabricating efficient electron injecting cathodes. Cathodes made with Al-LiF or Al-CsF composites are found to enhance the performance of organic light-emitting devices. With a composite cathode, devices based on an organic bilayer structure have shown lower operating voltage, higher efficiency and better forward light output than devices with LiF/Al, Mg or Al cathode. Unlike devices with Al and Li alloy cathode, OLEDs with composite cathode can be made with good reproducibility.

Invited lecture

**ADVANCES IN MOLECULAR, PHOTONIC AND DEVICE
ENGINEERING FOR NONLINEAR OPTICS AND
TELECOMMUNICATIONS**

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The maturing of a viable semiconductor compatible polymer based integrated optics technology based on thermally assisted electric field poling of functionalized polymers is currently opening a new avenue towards electrooptic devices for optical telecommunications. Nevertheless, various important requirements remain difficult to implement such as polarization independence or a quasi-phase matched periodic structure which cannot be readily ensured within the usual capacitor poling electrode configuration. We therefore propose and demonstrate alternative approaches which are able to meet these constraints while opening new challenging possibilities for future optical signal processing functions.

A first type of solutions is based on adaptations of the poled polymer technological track whereby a balanced sequence of a classical set of capacitive superimposed electrodes followed by co-planar transverse electrodes is designed and biased so as to ensure equal dephasing for the TE and TM projections of a randomly oriented incoming polarization. Alternatively, an oblique poling electrode configuration leading to a tilted average orientation, may ensure as much as a 80% yield for TE(TM mode conversion. Such a mode-converter, when inserted between a set of classical electrodes, can then also ensure polarization independence.

Whereas these experiments are performed at the vicinity of the glass transition, it is further possible to lower the process temperature down to room temperature by introducing coherent light beam interactions with the additional advantage of a localized imprint of the desired anisotropic or nonlinear pattern. Two basic types of approaches will be discussed in this perspective : one is based on the linear Weigert effect whereby a previously poled homogeneous structure can be locally randomized by shining an Argon ion laser through an adequately tailored mask, thereby leading to a periodic structure of possible use for quasi-phase matched nonlinear effects. We have also demonstrated the cooperative combination of a dipolar electric field coupling scheme with an Argon ion laser induced axial alignment leading to the demonstration of a waveguiding phase modulator poled at room temperature.

A further step, with possibly greater potential, is based on the more advanced “all-optical” poling approach which permits to “write” onto a film or any other type of pre-patterned

substrate, a linear or nonlinear susceptibility tensor with properties deriving from that of the writing beam polarization states. The most remarkable feature of this approach is the utilization of nonlinear phenomena, namely quantum interferences between different multiphoton absorption pathways coupled to photochemically or vibrationally driven relaxation modes, as a tool for imprinting sophisticated optical patterns. Moreover, we have investigated the coupling schemes of general 3-D multipolar molecules with adequately defined multipolar light beams capable of driving such molecules towards any refined statistical orientational pattern. Combining molecular and photonic engineering schemes may lead in principle to any desired spatial distribution of the optical susceptibilities. We will exemplify various early implementations of this approach in different areas pertaining to nonlinear optics such as polarization independent SHG films or TE-active electrooptic waveguides as well as parametric microcavities.

Invited lecture

**ORGANIC-INORGANIC HYBRID
MATERIALS FOR NONLINEAR
OPTICS APPLICATIONS**

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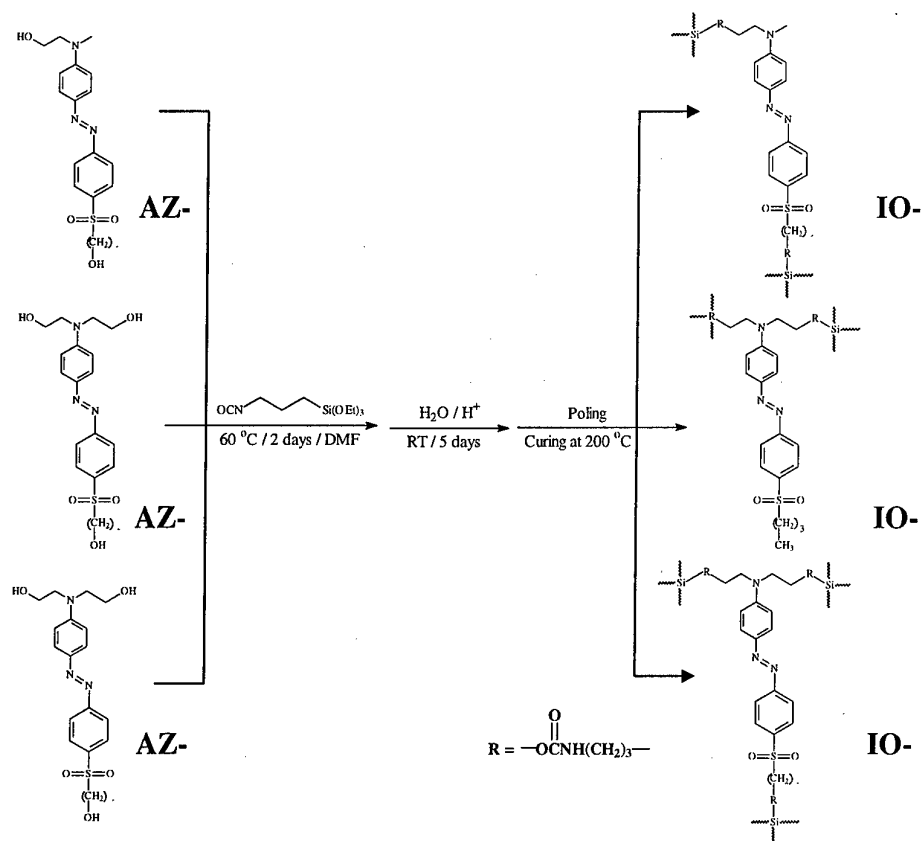
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Sol-gel processes have been intensively studied as a potential superior route for the preparation of ceramic, glasses and composites due to advantages and uniqueness of these processes compared to conventional melt and sintering techniques [1]. Using the sol-gel techniques, it is possible to make organic-inorganic hybrid materials as optical layers for photonics applications [2]

Most nonlinear optical chromophores have generally not been found to be good photonic media due to large absorption and high optical losses. Inorganic glasses, however, are excellent photonic media because of their high optical quality and extremely low optical losses. Therefore, combining inorganic glass and organic photo-functional molecules is one of the best ways to develop optical materials with large optical nonlinearity and low losses [3]. In addition to this, the use of highly cross-linked silica matrix can be remarkably reduced the thermal relaxation of the molecular dipoles [4].

Taking advantages of these, we have recently developed three different azosulfone dye/silica glass hybrid materials (Scheme 1). They are characterized as parallel (P), vertical (V) and parallel-vertical (PV), depending on bonding direction between the chromophore and the silica matrix. Each of their physical properties and nonlinear optical activity in terms of poling conditions is investigated. Also, the stability of a poling-induced dipole of three hybrids is compared. These hybrids are characterized by good temporal stability of optical nonlinearity, defect-free processability and controllable refractive index. Hence these systems may be potential materials for photonics applications

Scheme 1. Synthetic route for three types of organic-inorganic hybrid materials



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Invited lecture

FABRICATION AND PERFORMANCE OF MACH-ZEHNDER MODULATOR BASED ON ORGANIC-SILICA HYBRID FILMS

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Organic-silica hybrid materials have a number of advantages for nonlinear optical (NLO) applications over organic polymer systems; such as low optical propagation loss, temporal stability, chemical and mechanical stabilities. In order to overcome the relaxation problem of second-order NLO effect, we directed our attention to the organic-silica hybrid material, where NLO chromophores 4-[N,N-di-(2-hydroxyethyl)amino]-4'-nitrostilbene (DANS) and E-N-butyl-4-[2-{4[bis(2-hydroxyethyl)]aminophenyl}ethenyl]pyridinium tetra phenyl borate (BPTP) were attached to heavily crosslinked silica (SiO₂) network. Hybrid materials were synthesized by sol-gel process (Fig. 1) and thin films were fabricated by spin-casting method. Using Si²⁹ NMR spectroscopy, TGA, DSC, FTIR and UV/visible spectroscopy, chemical analysis for the film was performed and the basic physical properties such as refractive index and dielectric constant were characterized.

The NLO effect was established by the corona poling and DC contact poling methods. The poling efficiency depended on poling conditions such as poling temperature, poling time and applied voltage. The largest values of nonlinear optical and electro-optic coefficients obtained were $d_{31}=72$ pm/V at $\lambda=1.064$ μm and $r_{33}=16$ pm/V at $\lambda=1.3$ μm respectively. The poled film retained 95% of its initial r_{33} value after 800 hours at room temperature and 70% after 750 hours at 63°C. Relationships between the stability of NLO property and the poling conditions were studied extensively by investigating the dependence of second harmonic signals on temperature and it was found that the stability increased greatly as poling temperature became higher and poling time longer.

Utilizing the DANS hybrid material, a Mach-Zehnder light intensity modulator was fabricated. Fig. 2 illustrates the structure of the device. The device was fabricated on a silicon wafer on which Cr/Au was deposited as a bottom electrode. For the top and bottom claddings, a UV-cured epoxy was used with a typical thickness of 2 μm and the refractive index of the cladding was 1.546 at $\lambda=1.3$ μm . The core layer was made of the 2.1 μm thick hybrid film with refractive index of 1.610 at $\lambda=1.3$ μm . Photobleaching method was used to define the lateral cladding region and the cross sectional area of the core was 2.1×4 μm^2 . For DC contact poling, a gold electrode was deposited over the whole top surface and the film was poled at 110°C for 30 minutes under the electric field strength of 140 V/ μm . The dimension of the device was about 6.1 μm in thickness and 15 mm in length, respectively. The operational characteristics of the device were examined by using 1.3 μm laser diode.

Fig. 3(a) shows the single mode pattern of the device which was captured by CCD camera and Fig. 3(b) shows the intensity modulation response and an applied voltage. The half-wave voltage was about 13 V and the r_{33} value in the waveguide was estimated to be 10 pm/V.

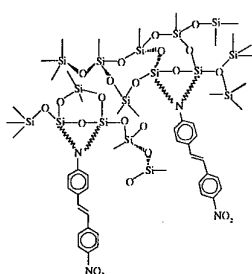


Fig. 1. Structure of the synthesized DANS-silica hybrid material.

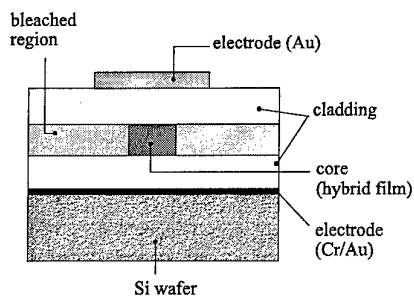
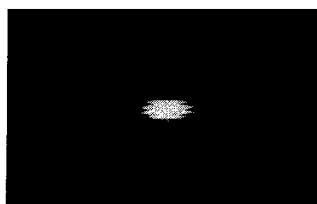
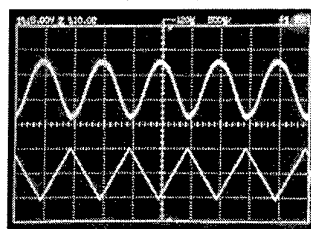


Fig. 2. A cross-sectional view of the Mach-Zehnder modulator.



(a)



(b)

Fig. 3. (a) TM_{00} single mode pattern and (b) intensity modulation response of the device.

Invited lecture

MOLECULAR ENGINEERING APPROACH TO DESIGNING ORGANIC NONLINEAR OPTICAL MATERIALS

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Organic nonlinear optical (NLO) materials continue to draw attention due to their potential application in laser frequency conversion, optical data storage devices, and optical communications. Therefore, there has been continued interest in the development of organic materials with desired NLO properties. Among the required materials properties appropriate for device applications are: (a) enhanced electronic NLO response, (b) low optical absorption, (c) high thermal stability. Generally, one or more of these properties are achieved via trial and error methods involving synthesis and characterization of potential organic materials. A rational way of developing organic NLO materials for device applications involves a molecular engineering approach based upon the knowledge of structure-property relationships. In this talk, I shall review recent developments in the quantum mechanical techniques to characterize structure-property relationships and their application to modeling new organic NLO materials. Results will be presented on several new optimized structures with promising second-order NLO coefficients.

Invited lectures

**SELF ASSEMBLED NANOSTRUCTURED CONJUGATED
SYSTEMS: PHOTOPHYSICS AND OPTOELECTRONIC DEVICES**

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Controlled order on the nanoscale range is a powerful approach, which was suggested by Richard Feynman already in the late fifties. By the technique of polymerizeable lyotropic liquid crystalline monomers, highly ordered poly(p-phenylene vinylene) matrix nanocomposites can be synthesized. The matrix is constructed with a polymerized saturated monomer system forming a hexagonal nanostructure of ordered hollow cylinders with center distances between 30 and 40 Angstroms. The center of these cylinders can be filled with single chains of conjugated polymers like poly(p-phenylene vinylene). We report on the crystal structure, photophysical properties (site-selective spectroscopy, photoinduced absorption and photoluminescence-detected magnetic-resonance) and the performance of electroluminescence devices of these new nanostructured conjugated materials.

Invited lecture

PATTERNING OF MICROSTRUCTURES IN POLYMERS USING PHOTO-INDUCED MOLECULAR MOTIONS

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Photoinduced molecular motions can be used to create molecular order. This is a key issue for the optimization of semi-conductor and optoelectronic devices. We discuss various situations in which the internal relaxation of photo-excited molecules make them work as optically driven motors. We illustrate this principle by the patterning of $\chi^{(2)}$ gratings and surface relief gratings using nonlinear interferences with appropriate combinations of laser beams.

Invited lectures

THE INFLUENCE OF THE MELT BLENDER ON PROCESS PARAMETERS IN INJECTION MOULDING OF ABS

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A perfectly homogenous melt is one of the prerequisites towards meeting increasingly strict quality requirements in the injection moulding. Melts can display heavy inhomogeneities downstream of the screw, including radial temperature differences and irregularities in pigment or additive distribution. This can lead to colour striation, staining, and discrepancies in the weight of products.

In the injection moulding the homogeneity of melts after they leave plastifying unit is often inadequate. It is recommended to use static mixing units in the flow channel between the plastifying unit and the nozzle to improve homogenization.

In this work we studied the influence of Sulzer's SMK-X mixer on temperature homogenization and colour distribution in the injection moulding of acrylonitrile butadiene styrene copolymer (ABS). Series of experiments were carried out with and without mixer on the Klockner F40 injection moulding machine. The mixer was located in front of the nozzle. The design of experiment technique was applied to minimize the number of required experiments. Barrel temperature, concentration of masterbatch, injection speed and cycle time were varied and quality of products tested by spectrophotometric measurements of colour difference and mass measurements.

The results proved that introduction of Sulzer's mixer had great impact on product aesthetic quality due to better temperature homogenization and colour distribution. Optimization of the process parameters has been done. Barrel temperature was reduced from 235°C to 227°C and this resulted in shorter cycle time of product production. This also shortened the down time of the machine in the case of mould change or maintenance. The better colour distribution, measured by colour difference of standard and product, was obtained with the Sulzer's mixer.

**RHEOKINETIC STUDIES OF CONCENTRATED HIGH
MOLECULAR WEIGHT EMERALDINE BASE
IN N-METHYL-2-PYRROLIDINONE SOLUTIONS
CONTAINING 2-METHYL-AZIRIDINE**

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Concentrated solutions of ultrahigh molecular weight emeraldine base (EB) are obtained when near stoichiometric quantities of 2-methyl-aziridine (2MA) per polymer repeat unit are co- dissolved in N-methyl-2-pyrrolidinone (NMP). Hydrogen bonds are formed between the secondary and tertiary EB nitrogen atoms of the polymer repeat unit, and both the 2MA additive and the NMP solvent molecules. The rheological behavior of such solutions is quite different from that of EB/NMP solutions without the addition of 2MA. The principals of rheokinetic analysis are used to investigate the mechanism of the EB*2MA complex formation in the concentrated EB/NMP/2MA solvent systems. The reaction rates, equilibrium constants and activation energies associated with these complexes are determined. Further, the stability of variable 2MA/EB molar composition and the kinetic effects due to variable temperature are reported for 20% (w/w) EB solutions. Highly electrically conductive polymers are easily formed from these solutions posses excellent physical properties.

INTERFEROMETRIC AND FOURIER TECHNIQUES FOR MEASUREMENTS OF OPTICAL PROPERTIES OF FIBRES

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The paper describes unique automated methods for measurements of textile fibres birefringence based on the interference pattern. The measurement of the birefringence of polymers and synthetic fibres provides information about their physical and chemical properties particularly about the degree of orientation of molecules, structural homogeneity and crystallinity. This knowledge is particularly useful for technologists in context of evaluating the effectiveness of the manufacturing process.

The most important problem of any interferometric method is evaluation of the interference order of fringes in the image of an object. Pluta's contribution in this field is well known as the VAWI technique family. These methods consist in using monochromatic light with continuously variable wavelength. For certain selected wavelengths interference fringes displaced by an object under study become consecutively coincident and anticoincident with the reference (undisplaced) fringes. Knowing the wavelengths and observing order change it is possible to calculate refractive indices and birefringence.

The technique based on optical Fourier transform pattern (OFT) is- unexpectedly, to some extent-a modification of the classical VAWI family. When a polarizing microscope equipped with the slit-diaphragm condenser is used and the specimen of the fibre is placed diagonally between crossed polars a characteristic pattern of circular fringes is observed in the back focal plane of the microscope objective which was first discovered by Pluta in 1981. The fibre behaving as a bifocal lens is the source of two spherical waves of slightly different curvature. The waves interfere producing an axially symmetrical pattern of fringes. The output pattern which is in fact a Fourier transform contains fringes of negative orders. Zero-order fringe is beyond the edge of the exit pupil and is never visible. The automatic analysis of the fringe pattern at different wavelengths enables to determine interference orders of fringes and the spectral birefringence. During measurements the wavelength is controlled using a Liquid Crystal Tunable Filter (LCTF), which is a new sophisticated device.

The paper demonstrates relation between both methods showing their similarities, advantages and disadvantages including theoretical description of the phenomena. In particular, aspects of automation, software and sources of errors are considered. The OFT technique is described wider since it is less known and the author's contribution in this field is much more significant.

NEW COMPOSITIONS FROM PHOTSENSITIVE COPOLYMERS FOR INFORMATION PROCESSING AND STORAGE

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In this work we present a number of new compositions from photosensitive copolymers for information processing and storage.

A number of donor-acceptor systems from carbazoly containing polymers, in particular from carbazolyethylmethacrylates (CEM) and oktylmethacrylates (OM) copolymers sensitized by threennytrofluorenone (TNF) derivates and additives of photochromatic substances from indolynospirobenzpyran row are investigated. Is established, that donor-acceptor systems as photoplastical layers put on a conducting basis have a photosensitivity $10^{-3} - 10^{-4} \text{ J/sm}^2$. The introduction in photoplastical layers 6-10 % of the photochromatic additives is increased by photosensitivity of donor-acceptor systems in 5-6 times. The especial growth of photosensitivity is observed in blue-green area of a spectrum. The greatest sensitization effect has 8'-nitro-1,3,3-three methylindolynospirobenzpyran. The occurrence of a strip of absorption (500-600 nm) in seen area of a spectrum testifies to amplification of donor-acceptor groupings in photoplastical layers and from here appreciable increase of photosensitivity.

The appreciable sensitization effect is reached at drawing of photoplastical layers on an injection films from chalcogenide glass semiconductors, for example from As_2Se_3 . Developed on the basis of photopolymer CEM:OM donor-acceptor systems have photosensitivity 10^{-6} J/sm^2 at 80-85°C, that on 2-3 order is higher than usual systems without injection. From received compositions of photopolymers were obtains photothermoplastical carriers for registration optical information.

A detailed experimental study of the kinetics of photodarkening and photobleaching in photochromatic polymer films is presented in this work. As a photochromatic polymer films we have obtained photochrom 1,3,3-three methyl-6(8)-nytroindolynospirobenzpyran in butylmetachrylat-styrol copolymer, which were taken in different percentage correlation. Optical transmission of the virgin samples on glass substrate and of the samples after irradiation has been measured as a function of wave length in the region from 0.33 up to 0.83 microns. The degree of photobleaching and the position of maximum of optical transmission depends of the composition and chemical structure of photochromatic polymer films. The influence of aging time has been investigated up to 24 hours. The rate of decrease of photobleaching depends on the compositions of photochromatic polymer films. The stability of photochromatic layers to UV-irradiation has been investigated. On

the base of this results were elaborated the information media for holographic image registration with resolution up to 5000 mm^{-1} .

In this work we present also the results concerning the possibilities of strengthening of polymer media with the scope to improve mechanical properties of the relief image (hardness, strength, adhesive stability) and the possibilities to make copies by hot stamping method. With the view to facilitate the multiplication of relief hologram copies, which were initially recorded on chalcogenide glass semiconductors or other registration media, the images were transferred by method of hot stamping on the thermoplastic layers. This layers were prepared from copolymers or other compositions, which contain chemically active liaisons of 4-aminostyrol or hlycedilmethacrylat. The thermoplastic layers with relief images can be cross-linked under the action of UV-light or under the action of chemical agents, for example, the ephyrat BF_3 vapor. As a result the polymer layers with the relief image become mechanical hard, strength, adhesive stable, without solubility in organic solvents (toluol, chloroform) and with stability to high temperature (up to 100°C). The second polymer matrix on the 4-aminostyrol and hlycedilmethacrylat thermoplastic layers can be used for the multiplication of the copies on the special thermoplastic material, prepared on the base of butadiene copolymers on which we can get up to 100 copies without significant changes of its characteristics.

INCIDENT ELECTRON ENERGY AND DOSE EFFECT ON OPTICAL PROPERTIES OF MODIFIED POLYVINYL CHLORIDE

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In polyvinyl chloride (PVC), subjected to irradiation with a beam of monoenergetic electron in a linear accelerator, the dependence of optical properties on the incident electron energy E and the dose ϕ were investigated. This was accomplished using UV-technique in the wavelength range 400-1200 nm. An attempt has been made to correlate the electron beam damage of PVC and the corresponding changes in optical parameters (e.g. the absorption coefficient α , band tail width ΔE , and indirect E_{op}^i and direct E_{op}^d energy gap). It is found that, the radiation induce effect may be visualized as three stages phenomena: Oxidative degradation, cross-linking and polymer scission. Stopping power of electrons and effective cross-sections for displacement of the various atomic species in PVC were calculated. Analysis of experimental results permits the conclusion that the changes in optical properties of PVC are due essentially to defects created in ionizing process, direct collisions of incident electrons with lattice atoms and multiple atom displacement.

*Corresponding author

SPECTROSCOPIC INVESTIGATIONS OF POLYANILINE COMPLEXES WITH SELECTED LEWIS ACIDS

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In the past 20 years more than 8000 papers devoted to polyaniline (PANI) doped (protonated) with Brönsted acid have been published. In particular new functionalized acids improving solution processibility of PANI have been tested. However polyaniline exhibits an interesting Lewis acid-base chemistry which has not been exploited to date. It is known that by complexing with appropriate Lewis acids, stiff backbone polymers such as aromatic poly(azomethines) can be solubilized in acetonitrile or nitromethane. We were tempted to verify whether this processibility improving method can be applied to polyaniline. For this reason we studied complex formation between PANI and SnCl_4 or FeCl_3 . When treated with a Lewis acid polyaniline readily dissolves in CH_3NO_2 or CH_3CN . The solutions have film-forming properties. Freestanding films of complexed PANI can be obtained by evaporation of the solvent. Elemental analysis shows that each molecule of the Lewis acid, when entering to the polymer matrix, is solvated with one molecule of the solvent. UV-vis-NIR spectroscopy indicates significant charge delocalization in the doped polymer, which is manifested by a broad absorption band extending towards the near IR. The solid films were additionally characterised by ^{119}Sn and ^{57}Fe Mössbauer spectroscopy. To a first approximation the Mössbauer spectra can be interpreted as originating from two types of complexes co-existing in equal amounts in the polymer. This finding is consistent with two types of complexing centers in polyaniline, namely amine and imine nitrogen. The intensity of the spectra significantly increases on lowering of the temperature, which seems to indicate a significant mobility of the inserted molecules at temperatures close to RT.

ORGANIC COMPOSITES EXHIBITING METALLIC CHARACTER: PREPARATION, STRUCTURE, PHYSICAL PROPERTIES

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Creation of non-traditional organic materials which possess good conducting properties is an interesting and important aspect of contemporary molecular engineering. Synthesis and characterization of conducting composites obtained by direct solid-solid charge-transfer reaction between electron donor and acceptor molecules [1] have been presented. Although these materials show great practical importance, their physical properties are not sufficiently known [2, 3]. Our interest is concentrated on materials originated from tetrathiafulvalene (TTF) - derived donors. It was shown that the composites based on this bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF) form especially interesting and promising group of new organic solids. The composite of this donor molecule and iodine exhibits metallic character and shows physical properties similar to the properties of the crystalline organic metal β - (BEDT-TTF)₂I₃. The UV-VIS-NIR-IR spectra of the composites are discussed with respect to their electrical, structural and magnetic properties. Some important spectral and transport parameters have been evaluated and discussed.

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QUANTUM MECHANICAL INVESTIGATION OF PHOTOACTIVE SUPERMOLECULES AND DESIGN OF MOLECULAR MOTORS AND LOGICAL DEVICES

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Two variable anisotropic random-walk stilbene based molecular motor device is designed from carbazole (Cz), 1,4-phenylenediamine (PhDA), stilbene and TCNQ molecules joined with $-C_2H_2-$ fragment bridges. The geometry optimization of bistilbene molecule was done by HF/6-311G**, stilbene molecule was optimized by DFT B3PW91/6-311G** and that was the basis for the design of stilbene based random-walk molecular devices. The planes of phenyl rings are approximately 13.36 degrees twisted in ground state and stilbene molecule becomes planar in first excited state by using *ab initio* configuration interactions single-excitation (CIS) method. It should be possible to excite two variable random-walk molecular device by two different wavelengths which correspond approximately to wavelengths of single Cz and PhDA molecules investigated by CNDO/S-CI and ZINDO-CI methods. After the excitation, this supermolecule should be deformed by two different ways and after electron tunnelling to acceptor fragment TCNQ this molecule should dissipate the energy moving on the surface by two different ways. Another kind of two variable random-walk device is designed based on one electron donor fragment and two electron acceptor fragments: Cz- $C_6H_5-CH=CH-C_6H_5$ -TCNQ, $-NO_2$.

Three variable anisotropic random-walk stilbene based molecular motors are designed by two ways. Cz, PhDA, N,N,N',N'-tetramethyl-1,4-phenylene-diamine (TeMePhDA), stilbene and TCNQ molecules joined with $-C_2H_2-$ fragment bridges or in another way: Cz- $C_6H_5-CH=CH-C_6H_5$ -TCNQ, TCNB, $-NO_2$. Four variable anisotropic random-walk stilbene based molecular motor device is designed from Cz, PhDA, stilbene, TCNQ and TCNB molecules joined with $-C_2H_2-$ fragment bridges. Six variable anisotropic random-walk stilbene based molecular motors are designed as: Cz, PhDA, TeMePhDA, stilbene TCNQ and TCNB molecules joined with $-C_2H_2-$ fragment bridges or: Cz, PhDA- $C_6H_5-CH=CH-C_6H_5$ -TCNQ, TCNB, $-NO_2$.

We have calculated DR1 azo dye molecule: $NH_2-C_6H_5-N=N-C_6H_5-NO_2$ (P. Lefin et al., Pure Appl. Opt., 1998, vol. 7, p.71). Geometry optimization was done using DFT B3PW91/6-311 model in ground state. The angles

C-N=N of optimized molecule are approximately 114 and 115 degrees. In this molecule weak bonds exist between bridge nitrogen atoms and those hydrogen atoms which are the

closest to phenyl ring - something like intramolecular hydrogen bonds. These intramolecular hydrogen bonds keep molecule in almost one plane: only 0.015 and 0.005 degrees are between the planes and -N=N- bridge. Also a relatively large charge transfer occurs from donor -NH₂ part to acceptor -NO₂ part: up to 0.12 electron charge in the ground state. That means that this derivative possesses a charge transfer band in the excited state. We have optimized the azo-dye molecule in the first excited state by using CIS RHF/STO-3G. Results show that the C-N=N angle changes from 115.5 to 123.5 and from 114.1 to 121.9 degrees. This indicates that intermolecular hydrogen bonds almost break during the excitation, while molecule remains in one plane.

On the ground of DR1 azo dye calculation results, several variable random-walk molecular motors were designed: two variable ones Cz, PhDA-C₆H₆-N=N-C₆H₆-NO₂ and Cz-C₆H₆-N=N-C₆H₆-TCNQ, -NO₂, three variable ones: Cz, PhDA, TeMePhDA-C₆H₆-N=N-C₆H₆-NO₂ and Cz-C₆H₆-N=N-C₆H₆-TCNQ, TCNB, -NO₂, four variable ones: Cz, PhDA-C₆H₆-N=N-C₆H₆-TCNQ, -NO₂ and six variable ones: Cz, PhDA, TeMePhDA-C₆H₆-N=N-C₆H₆-TCNQ, -NO₂ and Cz, PhDA-C₆H₆-N=N-C₆H₆-TCNQ, TCNB, -NO₂.

Molecular implementation (MI) of carbon-based two, three, four variable logic functions, summators of neuromolecular networks, cells of molecular cellular automata, molecular trigger – molecular logic devices and molecular devices for electronic genome regulation were designed on the ground of results of semiempirical quantum chemical calculations of above mentioned electron donor, electron insulator, electron acceptor and fullerene molecules. Complete set of sixteen MIs of two variable logic functions (for example: OR, AND, Implication, Equivalence, Difference, etc.) was designed and also proposed using MIs of two variable molecular logic function initial basic sets: {OR, AND, Negation} or {NOR} and, or {NAND}. We have described in detail the designed MIs of: a) two variable logic functions OR, NOR, AND, NAND (from fullerene molecules), Converse Unitary Negation-1, Converse Unitary Negation-0, Unitary Negation-1, Unitary Negation-0, "0" and "1" Matrix Constants; b) three variable logic functions AND, NAND, OR, NOR analogs; c) four variable logic functions OR, NOR, AND, NAND analogs. The electron jump via the insulator bridges in the supermolecules: electron donor-bridge-electron acceptor phenomenon was investigated by using CNDO/S-Configuration Interaction method.

We have investigated in detail the electronic structure of above mentioned planar electron donor and electron acceptor molecules, series of fullerene C₆₀ substituted derivatives: C₆₀CH₂, C₆₀C₂H₄, C₆₀C₃H₆, C₆₀C₄H₈, electron donor-bridge-electron acceptor diodes, and triodes using *ab initio* MP2, HF and DFT methods and designing new series of more correctly carbon-based MIs of two variable logic functions: OR, NOR, AND, NAND (two sets: one from planar molecules and another from fullerene molecules), Converse Unitary Negation-1, Converse Unitary Negation-0, Unitary Negation-1, Unitary Negation-0, "0" and "1" Matrix Constants based on geometry optimization procedure in ground and excited state molecular logic devices.

The quantum chemical calculations and investigation of benzene (Ph), Cz, TCNQ and PhDA molecules were performed using DFT BPW91 and B3PW91 models in cc-pVTZ basis sets with full optimization of geometry. The calculations of molecular diads designed from the above mentioned molecules and bridges: -C₂H₂-, -N=N- were carried out using B3PW91/6-311G and Hartree-Fock/6-31G. The design of molecular photoactive diade PhDA-C₂H₂-Ph was based on the analysis of quantum characteristics of Ph and

PhDA molecules. The results of optimization of interatomic distances and angles of molecular insulator bridge $-C_2H_2-$ showed that planes of PhDA and benzene molecule fragments are oriented by 1.18 and 1.92 degrees, respectively, towards the plane of the bridge fragment. Small negative charge equals to 0.03 e transfers from PhDA molecule fragment to the $-C_2H_2-$ and benzene molecule fragments. Therefore it can be expected that the electron charge should be transferred from PhDA fragment to benzene fragment during the diade excitation by light. The small charge transfer in the ground state exists because of large value of population of overlapping between C atoms of bridge fragment. Calculations of the diade spectrum using CIS Hartree-Fock method in 6-311G basis set in the first excited state showed that the diade should be excited by wavelength equal to 282.31 nm. This enables to use this molecular diade for the solar energy carbon-based converters.

Two supermolecules were designed using our results of quantum chemical calculations:

1) PhDA- N_2 -TCNQ- C_2H_2 -TCNQ- N_2 -Cz and 2) Cz- N_2 -TCNQ- C_2H_2 -Ph- C_2H_2 -Ph- C_2H_2 -PhDA. Depending on conditions of excitation and the output of transferred electron charge the (1) supermolecule can be Converse Unitary Negation-1, Converse Unitary Negation-0, Unitary Negation-1 or unitary Negation-0 two variable logic functions. The (2) supermolecule can be And, Nand, «0» as well as «1» Matrix Constants depending on the way of excitation and outputting the transferred electron charge.

The molecular logical devices joined to multivariable anisotropic random-walk molecular motors possess a possibility of moving when exposed to light and represent a new kind of intellectually controlled motors. The examples of such molecular logic motors designed are: 1) PhDA- N_2 -TCNQ- C_2H_2 -TCNQ- N_2 -Cz--TeMePhDA- C_6H_6 -N=N- C_6H_6 -TCNQ, -NO₂. Depending on conditions of excitation and the output of transferred electron charge the 1) supermolecule can be Converse Unitary Negation-1, Converse Unitary Negation-0, Unitary Negation-1 or unitary Negation-0 two variable logic functions and it possesses a possibility to move as two variable random-walk molecular motor. The 2) supermolecule Cz- N_2 -TCNQ- C_2H_2 -Ph- C_2H_2 -Ph- C_2H_2 -PhDA--TeMePhDA- C_6H_6 -N=N- C_6H_6 -TCNQ, TCNB, -NO₂. can be And, Nand, «0» as well as «1» Matrix Constants depending of the way of excitation and outputting the transferred electron charge and it possesses a possibility to move as three variable random-walk molecular motor.

OPTICAL PROPERTIES OF POLY-2-VINYLPYRIDINE-C-BLACK COMPOSITES

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Samples of 2-vinylpyridine oligomer and polymer were hot-pressed with different percentage of c-black (wt%). The diffused reflectance of polymer c-black, oligomer-c-black composite and polymer-CH₃I complex was measured at room temperature in the wave length range from 500 to 1800 nm. The energy gap of these different samples is decreasing with increasing c-black percentage.

Keywords: 2-vinylpyridine oligomer, poly-2-vinylpyridine, optical properties, semiconductors.

FROM POLYMER TO CERAMICS: LOW COST MANUFACTURING OF CMC MATERIALS

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High performance ceramics are still largely produced via powder routes. The main disadvantage of these materials is their brittle failure behaviour and the thus dissatisfactory damage tolerance of ceramic components. The most favourable way to improve the fracture toughness of ceramics is the introduction of thermally stable continuous fibres.

Different processing techniques are currently in use for the development and prototype production of fibre reinforced ceramic matrix composites (CMC). Long manufacturing times, multiple reinfiltration steps and expensive raw materials lead to high material prices which have prevented their breakthrough to terrestrial applications up to now. To overcome these restrictions and widen the applicability of CMCs - in particular, to enter in fields of mechanical engineering - a novel cost-efficient manufacturing route has been developed by DLR.

The processing starts with the manufacture of carbon fibre reinforced plastic composites (CFRP) with matrices of high carbon content. Normally commercially available resins like phenolics or other aromatic polymers are used to fabricate laminates by common CFRP techniques like resin transfer moulding (RTM), autoclave pressing or filament winding. These green bodies are produced near net and in simple shapes like rings, disks, panels or tubes.

After curing, the CFRP green bodies are heat treated under nitrogen atmosphere. During this pyrolysis step, the polymer matrix is converted to an amorphous carbon matrix. A translaminal microcrack system of high capillarity arises through matrix shrinkage, resulting in an open porosity of 15 - 30 %. The macroscopic shrinkage of the green body depends on the type of polymer, the fibre/matrix bonding forces and the fibre content. For bidirectional reinforcements no macroscopic shrinkage occurs in the fibre direction. Perpendicular to the fabric plane the linear shrinkage usually lies in the range of 2 - 10 %.

In the final processing step - siliconization - the crack system is infiltrated with molten silicon via capillary forces and this reacts with the carbon matrix to form silicon carbide (SiC). The composition of the resulting C/C-SiC composite is strongly dependent upon process parameters. In general, however, the material is characterized by a high proportion of load bearing carbon fibres with the internal volumetric protection of SiC.

Generally, the CMC materials that are manufactured via this liquid silicon infiltration process (LSI) can be characterized with:

- Excellent thermal shock resistance
- High mass specific properties
- Short processing times

Taking advantage of the simplicity of the LSI process and the low raw material costs, C/C-SiC components offer a wide range of possible applications. Very complex C/C-SiC structures have already been realized and demonstrate the transferability of the material's characteristics from samples to real components. Within industrial cooperation, C/C-SiC materials are being developed as friction materials for weight saving brake construction. The prototypes currently under investigation cover the whole range of application fields - from high performance clutches and brakes to ultralight brake disks of future lightweight vehicles. Further prospective products like bearings, jet vanes or high performance tools show that C/C-SiC materials are a new material class which is also feasible in special fields of mechanical engineering.

This paper deals with the actual status of the material's development and shows new applications where C/C-SiC composites are attractive alternatives to conventional materials.

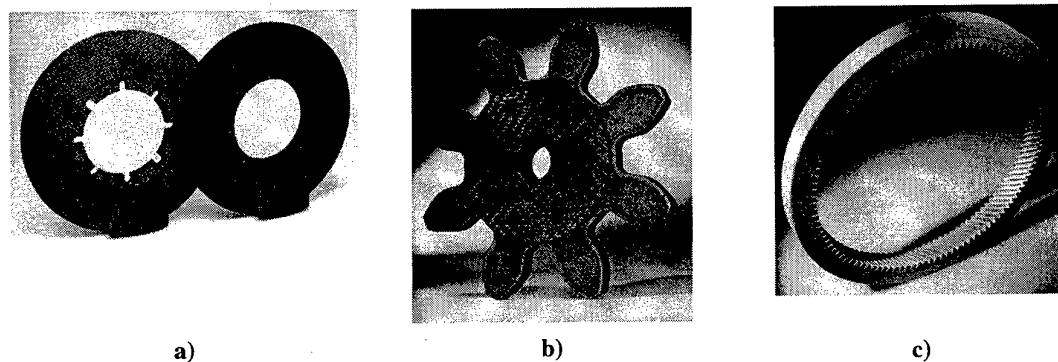


Figure 1: Prototypes of C/C-SiC materials for different applications

- a) Brake disks and pads for automotive vehicles (Ø 280 mm)
- b) Lightweight gear wheel, each tooth with the same fibre orientation
- c) Honing tool for the surface finishing of metals

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SELF-STABILIZED STYRENE POLYMERS

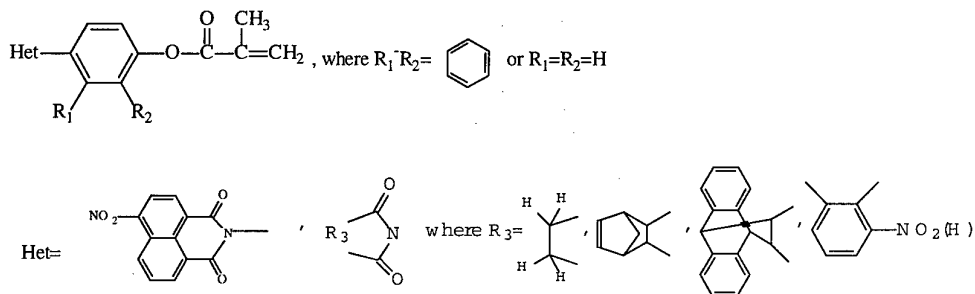
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“Doping” monomers - substituted phenyl- and naphthylmethacrylates were proposed for self-stabilization of styrene polymers.

Some kinds of new monomers based on aminophenols and aminonaphthols - acylaminophenyl-methacrylates, phenyl and naphthyl methacrylates substituted in 4-position by different nitrogen containing heterocyclic systems of such structures:



have been synthesized and studied by analytical and spectral methods.

Styrene polymers and copolymers containing small quantities of these monomers in the polymer chain were obtained by methods of radical polymerization. The influence of such intrachain additives on destruction processes were studied by the thermogravimetric analysis and their stabilization and antioxydant action was proved. The most strong action has units of additives with naphthalimide fragment. The photooxydative destruction in polymer films was studied by irradiation of complete UV-light. The effect of photostabilization was observed for styrene copolymers with imidonaphthyl methacrylates, especially with phthalimide rings.

The new advanced materials have been developed for electronic industry based on studied polymers.

ELECTROOPTICAL CHARACTERIZATION OF VARIOUS PDLC MATERIALS

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Polymer Dispersed Liquid Crystal (PDLC) composites have attracted great attention recently because of their wide applicability. The composites can be prepared by various methods (1) of the liquid crystal induced phase separation in the form of micron size droplets dispersed in a polymer matrix from a homogeneous solution of the two-component system:

1. polymer / liquid crystal in molten state;
2. monomer or prepolymer / liquid crystal in liquid state;

or the three component system:

1. polymer / liquid crystal / common solvent;
2. polymer / liquid crystal / polymer solvent.

However in the last method the liquid crystal initially forms a separate phase as an emulsion in the polymer solution.

The above mentioned methods were applied to obtain various PDLC materials (2-5). It was found that the PDLC materials obtained by the photopolymerization-induced phase separation method with liquid crystal droplets formed from the oligoester resin / liquid crystal (nematic mixture W-52) homogeneous solution presented the best electrooptical properties.

The phase separation kinetics and the phase diagrams were measured and calculated. The electrooptical properties and switching results are found dependent on the method of PDLC films preparation influencing both their morphological structure and the stiffness of the polymer matrix (4).

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Inorganic - Organic Hybrid Composites

Invited lecture

ORMOCER®S*-INORGANIC-ORGANIC HYBRID MATERIALS FOR E/O-INTERCONNECTION-TECHNOLOGY

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Hybrid inorganic-organic polymers (ORMOCERs®) have been developed and tested for evaluation in optical and electrical interconnection technology. The photopatternable materials with negative resist behavior are composed of inorganic oxidic structures cross-linked or substituted by organic groups. They are prepared from organosilane precursors by sol-gel-processing in combination with organic crosslinking of polymerizable organic functions. As a result of these functionalities the properties of the ORMOCERs can be adjusted to particular applications. Systematic variation of composition combined with adaptation to micro system technology allows great flexibility in processing. The main features of these materials are:

- Combined use as dielectric and passivation layers in electrical systems and devices as well as core and cladding for optical applications enables e/o applications with high integration levels.
- Postbaking at moderate temperatures (120-170°C) enables processing on low-cost substrates such as FR-4 and BT.
- Easily adaptable to thin film technology: spin-on with planarization >90% and via diameters down to 20 µm have been achieved.

Optical properties

- optical loss $\alpha = 0.23$ dB/cm at 1310 nm (not fluorinated!)
- refractive index (at 588 nm) = 1.52 (primary index tuning range)

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ELECTRICAL PROPERTIES

- permittivity ϵ_R at 10 kHz = 3.2
- dielectric loss at 1 MHz $\tan(\delta) = 0.004$
- volume resistivity $R_D \geq 10^{16} \Omega\text{cm}$

Thermal stability

- Despite moderate curing temperatures, the material withstands standard metallization and soldering process.

Demonstrators

Multilayer (e.g. 5 conducting and 4 dielectric layers) focusing on different applications were demonstrated on various substrate materials. Single-mode as well as multimode-type waveguides were manufactured and characterized.

Focus of this publication

Beside the chemistry of the new materials this invited paper will describe the focused modification according the technological needs as well as publishable parts of the established thin film technology. Finally a MCM-demonstrator and e/o-demonstrator based on ORMOCER-technology will be described.

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Invited lecture

REACTIVE ORMOGELS- NEW CLASS OF HYBRID MATERIALS FOR PHOTONICS

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A newly emerging class of inorganic–organic hybrids is presented as promising materials for passive and active components of photonic devices. Reactive (photopolymerizable) ormogels (organically modified gels) are inorganic–organic macromers equipped in reactive groups capable of heat or radiation induced polymerization. They are similar to reactive oligomers, components of UV-curable formulations, but differ in that their main backbone is inorganic in nature.

Strategies leading to the synthesis of reactive ormogels are discussed. They include:

- Hydrolytic and non-hydrolytic sol-gel processing of organosilanes
- Functionalizations of colloidal inorganic oxides
- Functional silylation of polymeric silicic acid

In admixture with organic monomers and/or oligomers, reactive ormogels constitute UV-polymerizable formulations, which can be easily designed to meet the requested properties of countless photonic applications.

Successful applications of these materials have been as UV-curable protective coatings and claddings for optical fibers, and host matrices for lasing dyes. Rare earth doping and UV-imprinted waveguides are also discussed. Currently, hybrids based on fluorinated polymer-silica derived from hydrolysis and condensation of functional organosilanes have proved to be efficient hosts for perylene based laser dyes. They also serve well as low refractive index, water repellent, and corrosion protective coatings for silica and plastic substrates.

Another example of active component material for photonic application is Erbium-Ytterbium doped POF, typically used as amplification devices in 1.55 μm optical communications. Some photosensitive ormogels, derived from silica-titania binary sol-gel glasses and having negative resist lithographic characteristics, have been used to produce good quality, low loss, imprinted ridge waveguides with or without gratings.

Titania –silica based ormogels have also been used to achieve high index coatings with gratings for γ -radiation array detectors.

Invited lecture

NEW UNSATURATED ORGANOSILICON POLYMERS VIA CATALYTIC POLYCONDENSATION OF DIVINYL – SUBSTITUTED SILICON COMPOUNDS

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Recent developments of ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) have opened new avenues for synthesizing a variety of polymeric materials including polymers possessing various functionalizations [1].

Many organosilicon oligomers and polymers prepared by metathetical activity of silicon containing dienes (but except divinylsubstituted silicon compounds) and cycloolefins with silicon-containing substituents (in the presence of traditional W, Mo and Re catalysts) find a potential application as membranes, adhesives, materials of special electrophysical, optical and thermal properties as well as precursors for ceramics, graft-copolymers and thermosetted and self-cured materials [1-3].

Our study on the polycondensation of divinyl derivatives of silicon compounds in the presence of ruthenium and rhodium complexes have allowed to find a new and an effective method for synthesis of unsaturated carbosilanes [4], carbosiloxanes [5] and carbosilazanes.

Under optimal conditions, polycondensation of divinyl dimethylsilane, divinyl tetramethyldisiloxane and divinyl tetramethyldisilazane gives silylene-vinylene, siloxylene-vinylene as well as silazanylene-vinylene oligomers, respectively.

The polymers have been identified by ^1H and ^{13}C NMR spectra as well as by DEPT method to detect a chain with trans-1,2 isomers as well as 1,1-disilyl(disiloxy, disilazyl) isomers. The presence of the latter confirms a non-metallacarbene mechanism for the polycondensation which is an evidence for the insertion-elimination mechanism. Diallyl di-organosilanes undergo polycondensation to give silylene-propylene oligomers prior to the isomerization of diallylsilanes followed by their heterocoupling with a parent diallylsilane [6].

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Invited lecture

METAL NANOCATALYSTS STABILIZED IN PROTECTIVE POLYMER MATRICES

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This review focuses on noble metal nanoparticles generated by reduction reactions within a polymeric, protective matrix. Of particular interest are particle characteristics such as sizes, size distributions, shapes, and morphologies, and how these important features depend on the metal precursor type, preparative conditions, and the nature of the protective polymer. If the polymer itself has a complex morphology, this can be exploited to control the location and distribution of the particles within the matrix. Phase-separated block copolymers are of considerable importance in this regard. Many of the systems thus prepared were evaluated for their catalytic activity using a standard hydrogenation reaction. Some evaluations were repeated after considerable storage times to characterize the shelf lives of these materials.

Invited lecture**NANOSTRUCTURED TWO-COMPONENT SOL-GEL MATERIALS****Ulrich Schubert**

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Aerogels have highly interesting physical properties due to their high porosity. A modification of the aerogel composition by incorporation of organic groups supplements the spectrum of properties with those provided by the organic groups. Monolithic inorganic-organic silica aerogels are prepared by base-catalyzed sol-gel processing of Si(OR)_4 / R'Si(OMe)_3 mixtures (R' = non-functional or functional organic group), followed by drying of the wet gels with supercritical CO_2 . Because the nanostructure of aerogels is very important for their physical properties, the control of the mutual arrangement of the organically substituted and unsubstituted building blocks is crucial. Sol-gel processing can be performed in a way that the microstructure of the obtained aerogels is the same as that of an unmodified silica aerogel prepared under the same conditions, and that the organic groups cover the inner surface of the aerogel network. This is achieved by a two-stage process in which the $\text{R'SiO}_{3/2}$ units condense to a pre-formed gel network obtained by hydrolysis and condensation of Si(OR)_4 .

Aerogels prepared from two-component alkoxide mixtures are an example for the deliberate ordering of the different groups during sol-gel processing by control of chemical parameters. However, the creation of nanostructures is also possible after the gels have been formed. When metal salts are reacted with silanes of the type $(\text{RO})_3\text{Si}(\text{CH}_2)_n\text{A}$, in which A is an organic group capable of coordinating to metal ions (mostly nitrogen-containing groups), and the resulting, in situ-formed metal complexes $[(\text{RO})_3\text{Si}(\text{CH}_2)_n\text{A}]_n\text{MX}_n$ are co-processed with Si(OR)_4 , homogeneous gels are obtained in which the metal precursor is dispersed to the highest possible degree. Controlled thermal treatment of these gels results in the growing of nanosized metal oxide particles. Reduction of the formed nanocomposites MO_y / SiO_2 by hydrogen yields metal/ SiO_2 nanocomposites.² The metal particles obtained by this approach are highly dispersed, not agglomerated and homogeneously distributed in the SiO_2 matrix, even in materials with high metal loading. The particle diameters are typically in the range $< 2 - 25$ nm, depending on the metal and the reaction conditions. The size distributions are very narrow, and the metal particles are accessible (e.g., if the composites are used as heterogeneous catalysts), because of the porosity of the silica gel matrix.

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ELECTROOPTICAL DEVICES FROM ORGANICALLY DOPED SOL-GEL MATERIALS

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Many papers have recently demonstrated that transparent matrices made by the sol-gel method are ideal as hosts for active photoactive or electroactive organic dopants. Sol-gel optics applications have recently reported about the importance of an adequate and precise control of the compositional and pore surface variations in the cage of trapped molecules, which is necessary to the preparation of novel optical and electrooptical gel-glasses.

In this lecture, gel-glass dispersed liquid crystal (GDLC) with electrooptical properties shall be presented as an application of the sol-gel process for trapping microdroplets of nematogenic organic compounds (i.e. liquid crystals, LCs). GDLC films may be used as electrooptical devices. Upon application of an external electric field, unaltered GDLCs were made to switch from white opaque to colorless transparent states. The different electrooptic features of GDLCs, including GDLC performances for color display applications shall be presented.

KEYWORDS: Gel-Glass Dispersed Liquid Crystals, GDLC, Electrooptic, Sol-Gel.

Invited lecture

BORON NITRIDE (BN) AS A HIGH TEMPERATURE MATRIX

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An oligomeric material based on borazine units has been shown to convert to BN in very high yield (90%). The oligomer can be used as a melt or solution to impregnate a carbon fiber lay-up. Heating to 1200°C yields a C/BN composite with outstanding mechanical properties. This was unexpected since the carbon fibers have a negative coefficient of thermal expansion while the BN matrix should be positive. What was postulated and subsequently proven was that the oligomer formed a discotic phase which tended to match the CTE of the fiber at the interface. Of equal importance the oxidation resistance of the C/BN is 850°C compared to 450°C for C/C composites. This property can extend the lifetime of C/C aircraft brakes by a factor of 5X.

In this presentation earlier work on C/C composites is briefly reviewed. Then recent progress on developing C/BN as a high temperature composite is described. Data are presented to a) demonstrate the liquid crystalline character of the oligomer, b) describe the thermal and mechanical properties of the C/BN composite, and c) show how the well-known instability of BN to moisture can be eliminated. Use of the BN matrix with inorganic fibers to yield composites with low observable features at elevated temperature is described.

Invited lecture

POLYMER-MODIFIED CERAMICS

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The term “Polymer-Modified Ceramics” will be defined. Major theme of this entry will be the synthesis and characterization of composite/hybrid materials in which the polymer is the dispersed phase, with the goal being of improving the properties of the host ceramic matrix. Discussion will be focused mainly on the materials that have strong interactions between the polymer (particularly vinyl polymer) and ceramic (particularly silica, alumina and titania) components such as extensive hydrogen-bonds and/or covalent bonds. Various synthetic routes will be reviewed with emphasis on the chemically or photochemically catalyzed sol-gel reactions under controlled conditions so that the polymer chains are uniformly dispersed in the inorganic/ceramic networks. The chemical, physical and biological properties of the polymer-modified ceramics will be described in relations to the nature and composition of the polymer and ceramic components. A number of potential applications will be presented. Some latest results from our laboratory might be included. A list of key reviews and references will be provided.

Invited lecture**ADVANCED PORE SYSTEMS THROUGH NANOCASTING**

**Christine G. Göltner, Beate Berton, Hans-Peter Hentze, E. Krämer,
Markus Antonietti**

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Aqueous lyotropic aggregate structures of amphiphilic block copolymers (ABCs) are utilised as templates for the generation of porous silicas in a process termed *Nanocasting*.¹ While heterodisperse templates afford considerably disordered mesoporous silica, low-dispersity ABCs allow the synthesis of made-to-measure pore systems. The lyotropic phases of monodisperse ABCs show a rich polymorphism, which is reflected in a large variety of pore sizes and architectures obtained. Suitable combination of templates results in hierarchical pore systems, e. g. silicas with bimodal pore size distribution.²

Not only can the pore structure be precisely designed via changing experimental parameters (see Fig. 1),^{3,4} but the method can also be applied analytically to the elucidation of lyotropic ABC phase structures.⁵

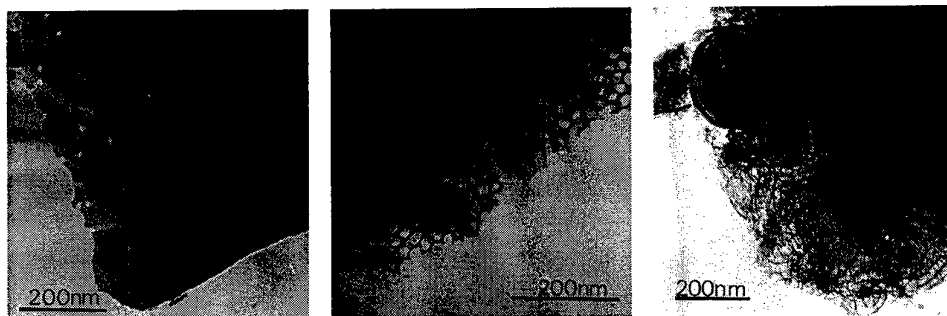


Fig. 1: TEM images of ABC-templated silicas: Density, shape and correlation of pores can be adjusted via the template concentration; left (20 % template): isolated bent cylinders, middle (50 %): hexagonally packed cylinders, right (70 %): collapsed lamellae.

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*Invited lecture***DESIGN OF HYBRID ORGANIC-INORGANIC NANOCOMPOSITES
SYNTHESIZED VIA SOL-GEL CHEMISTRY****C. Sanchez**Chimie de la Matière Condensée, UMR CNRS 7574, Université Pierre et Marie Curie
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The mild characteristics offered by the sol-gel process allow to introduce organic molecules or even bio-components inside an inorganic network. Inorganic and organic components can be mixed at the nanometric scale, in virtually any ratio leading to the so-called hybrid organic-inorganic nanocomposites. These nanocomposites can be obtained by embedding or grafting organic or bio-components within or to the inorganic networks obtained through hydrolysis and condensation reactions of metal alkoxides or organically functionalized metal alkoxide precursors. Numerous hybrid organic-inorganic materials have been developed in the past few years. This development yields many interesting new materials, with mechanical properties tunable between those of glasses and those of polymers, with improved optical properties (efficiency, stability, new sensors ..), with improved catalytic or membrane based properties. This field of materials research mainly rises from chemists skills and demonstrates the major role played by chemistry in advanced materials. The properties that can be expected for such materials depend evidently on the chemical nature of their components, but they also depend on the synergy of these components. Thus, the interface in these nano-composites is of paramount significance and one key point of their synthesis is the control of this interface. Design, synthesis and properties of hybrid organic-inorganic nanocomposites materials will be discussed on the basis of striking examples of hybrids made from modified silicon, tin and transition metal alkoxides. Finally a short outlook of the very promising field called "sol-gel chemistry of organized matter" will be presented.

*Invited lecture***ORGANIC-INORGANIC HYBRID MATERIALS WITH SPECIFIC SOLUTE AND GAS TRANSPORT PROPERTIES FOR MEMBRANE AND SENSOR APPLICATIONS****Christian G. Guizard**

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Organic/inorganic hybrid materials offer specific advantages for the preparation of artificial membranes exhibiting high selectivity and flux as well as good thermal and chemical resistance. Artificial membranes, organic or inorganic, can be classified in two main categories based on transport mechanisms. The first category involves porous membranes in which transport can be described by different mechanisms depending on pore size (viscous flow, Knudsen diffusion, molecular sieving). In the second category, membranes exhibit a homogeneous dense structure in which mass transport is described by a solution-diffusion mechanism. The presentation is concerned with the design of hybrid materials with the aim to produce membranes able to achieve selective transports of ions and small molecules from a liquid phase or gas molecules from a gas phase. Taking into account basic principles of mass transfer in homogeneous membranes, improvements on selectivity and flux are expected from the contribution of organic and inorganic parts in the hybrid membrane material.

Hybrid membrane materials can be classified in two categories:

- *Type I* in which only interactions like van der Waals forces or hydrogen bonds exist between organic and inorganic parts. Hybrid materials can be described here as micro or nanocomposites in which one part (organic or inorganic) is dispersed in the other part acting as the host matrix.
- *Type II* in which covalent bonding exists between organic and inorganic parts, resulting in an homogeneous hybrid material at the molecular level.

Both types can be applied to membrane preparation. Examples of *type I* and *type II* hybrid materials are presented. Dealing with *type I*, molecular sieves such as microporous silica beads or zeolite crystals have been added to polymer matrices as an attempt to increase gas separation membrane performance. Also, specific organic molecules have been inserted in a silica matrix as the active part of chemical sensors. Regarding *type II* materials, the arrangement at the molecular level of the organic and inorganic parts as well as their chemical composition have been investigated for facilitated transport of heavy metal ions

or aminoacids in aqueous media, but also for separation of oxygen, nitrogen or volatile organic compounds from air.

Processing of these membranes is mainly based on the sol-gel process for which the synthesis of hybrid materials is undoubtedly one of the major advances. The specific advantages of this “chimie douce” method (low temperature chemical process, large variety of material precursors, material structure adaptability, and coating process possibilities) are described here in relation with mass transport mechanisms in solid matrices as a very suitable way to design and synthesize artificial membranes with improved performance.

Invited lecture**BIO-ENCAPSULATION WITHIN SOL-GEL GLASSES**

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The sol-gel process opens new possibilities in the field of biotechnology. Sol-gel glasses are formed at room temperature via the polymerization of molecular precursors such as metal alkoxides. Proteins can be added to the solution of precursors. Hydrolysis and condensation then lead to the formation of an oxide network in which the protein molecule remains trapped. Small analytes can diffuse through the pores allowing bioreactions to be performed in-situ, inside the sol-gel glass. Trapped enzymes still retain their biocatalytic activity and may even be stabilized within the sol-gel cage. Moreover the transparency of sol-gel matrices makes them suitable for the optical detection of colored reactions. Sol-gel coatings or beads can be used for the realization of biosensors or bioreactors.

Whole cell bacteria can also be immobilized within sol-gel glasses. They behave as a “bag of enzymes”. The membrane of bacteria cells protects enzymes against denaturation and avoid their leaching during repetitive operations. *Escherichia coli* induced for β -galactosidase was immobilized within sol-gel glasses. Transmission electron microscopy shows that bacteria are randomly dispersed within the silica matrix and that their cellular organization is preserved. The β -galactosidase activity of entrapped *E. coli* was studied using p-NPG as a substrate. The formation of p-nitrophenol was followed by optical absorption. These experiments show that *E. coli* still exhibit noticeable enzymatic activity after encapsulation, even on dried xerogels.

Antibody-antigen recognition has been shown to be feasible within sol-gel matrices. Trapped antibodies bind specifically the corresponding haptens and can be used for the detection of traces of chemicals. Even whole cell protozoa have been encapsulated without any alteration of their cellular organization. For medical applications, parasitic protozoa have been trapped within sol-gel matrices and used as antigens for blood tests with human sera. Antigen-antibody interactions were followed by the so-called Enzyme Linked ImmunoSorbent Assays (ELISA).

Invited lecture

SIDE-CHAIN LIQUID CRYSTALLINE SILICON-CONTAINING POLYMERS

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SYNTHESIS AND PROPERTIES OF SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS OF REGULATED STRUCTURE WERE STUDIED.

SIDE-CHAIN SILICON-CONTAINING POLYMERS

We have been using silicon compounds in designing side-chain liquid crystalline polymers. The introduction of siloxane chains as side chains lowered the transition temperature. Recently, investigations focusing on liquid crystalline behavior of poly(carbosilane)s were published. We reported liquid crystalline polycarbosilane.

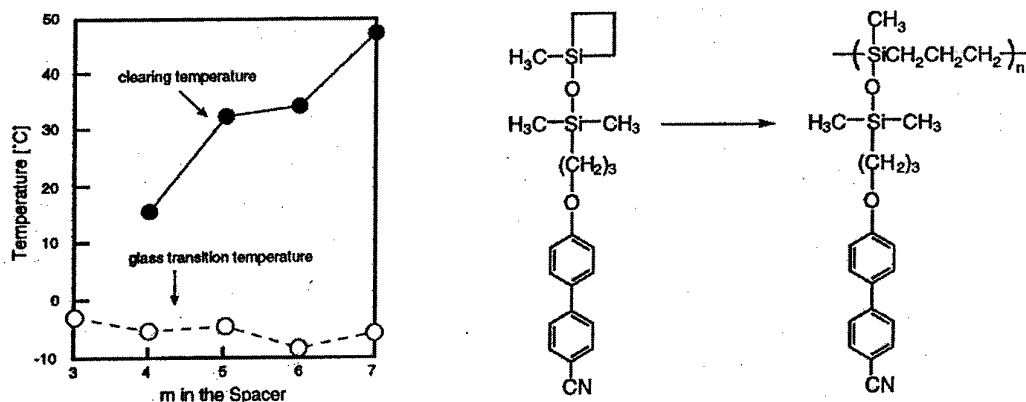
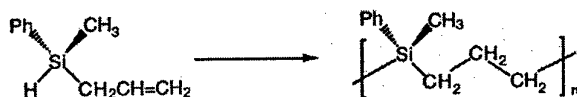


Figure 1. Dependence of m on the transition temperatures of poly(oxetane)s containing pendant disiloxanes.
 m : number of the methylene units in the spacer.

It is very important to control the stereochemistry of Si atom in the repeating units to correlate precisely such behavior with the primary structure of polymers. We designed a synthesis starting from optically active silanes.



Methyl(1-naphthyl)phenylmethylsiloxane is a useful and versatile starting material in the synthesis of variety of optically active silicon compounds.

Isotactic poly[(methylphenylsilylene)trimethylene] was synthesized from optically active allylmethylphenylsilane.

The 500 MHz ^1H NMR spectra of the polymers are shown in Figure 1. In the spectra, the SiCH_3 signal is split into three singlets at 0.120, 0.125 and 0.131 ppm reflecting the triad tacticity, which were assigned to the isotactic, heterotactic and syndiotactic triad, respectively.

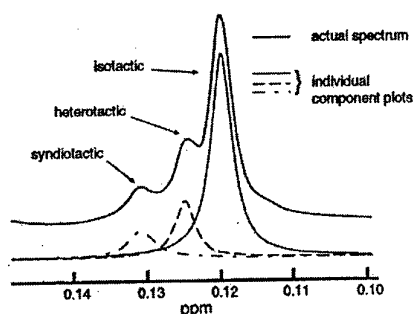


Figure 2. 500 MHz ^1H NMR spectra of CH_3 of 1

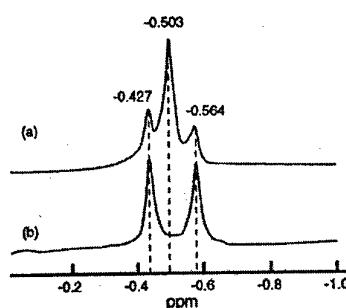


Figure 3. 75.4 MHz ^{13}C NMR spectra of $\text{Si}(\text{CH}_3)_2$ of 2

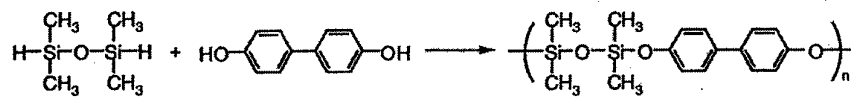
Related to this we could resolve 7-methyl-7-naphthyl-7-sila[4.2.0]1,3,5-octatriene, and obtained isotactic polymer. Although the optical activity of the starting monomer reflects in the isotacticity of the formed polymer via selective b-addition, the optical activity itself is lost in the polymer since the formed polymer is pseudo-asymmetric. In order to keep the optical activity in the polymer from the optical active monomer, it is necessary to distribute such optically active repeating unit connected with different constitutional unit in the polymer chain. Optically active vinylhydrodisiloxane and five-membered cyclic silicon compound, (S)-13, synthesized according to the Scheme 2, were chosen as monomer, and the polymerization reactions were studied.

^{13}C NMR spectra of $\text{Si}(\text{CH}_3)_2$ in the polymer obtained from racemic and optically active monomers are shown in Figure 2. Atactic polymer showed three peaks (-0.427 ppm, -0.503 ppm and -0.564 ppm), while the polymer from optically active monomer showed mainly two peaks (-0.427 ppm and -0.564 ppm).

Two methyl carbons in S-S (or R-R) diad are located in quite different environments and therefore have two chemical shifts. In the case of S-R (or R-S) diad, two methyl groups are in very similar environments, and their carbon r

esonances will appear at the similar position, i.e., methyl groups of S-R and R-S diads will appear as one inseparable peak. $\text{Si}(\text{CH}_3)_2$ in atactic polymer, therefore, would be split into three peaks (the central peak represents the S-R and R-S diads, two side peaks represent S-S and R-R diads) in the ^{13}C NMR spectrum, with an intensity of 1:2:1. While pure isotactic

polymer, containing only S-S (or R-R) diad, would show two peaks of methyl carbons, and pure syndiotactic polymer only one (S-R and R-S diads). The present polymer showed two distinct peaks of methyl carbons, indicating the polymer is highly isotactic.



FUNCTIONAL POLYSILOXANES – SYNTHESIS, PROPERTIES AND APPLICATIONS

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Poly(methyl)siloxanes in form of fluids, resins or elastomers are by far the most important commercial silicon based polymers and the most popular organic derivatives of inorganic polymers of 20th century. Thousands of useful applications of silicones, due to their intrinsic properties, have been developed during the last fifty years [1].

Introduction of a specific organic function on the polysiloxane chain or at its ends has opened new fields of applications which are a result of siloxane chemical reactivity and some added values like solubility in water, miscibility, paintability, lubricity etc [2]. Such silicones are usually synthesized via ring opening (co)polymerization, co-polymerization of linear siloxane monomers and macromonomers, hydrosilylation of poly(methyl, hydro)siloxanes as well as organic modification of the other functional siloxanes [2]. Besides, hydrosilylation process is often applied for preparation of appropriate monomers, modification of polyolefins, hydrosilylation polymerization as well as curing of siloxanes [3].

The most popular amino, epoxy, carbinol, carboxyl, acrylate and methacrylate substituted silicones due to a different reactive organic function can react with a variety of polymers and have been widely applied in composites, paints, textile finishing, electrical and microelectronic applications and were frequently used as lubricants or surfactants. Side chain liquid crystal polysiloxanes have been synthesized for more than 20 years using mainly olefinic mesogens attached to flexible polymer backbone. Some polymers with non-hydrolyzable functionality (polyether, mercapto, alkyl, alkoxy, fluoroalkyl groups) have found a vast number of applications in specialty composites, protective coating, personal care as well as specialty lubricants.

Additionally, functional siloxanes are blended with organic polymers providing their new properties and improving their performance in so-called silicon enabling technologies [1]. Functional siloxanes without a doubt will follow 20th century silicones career as new silicon based materials in the up-coming century.

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ULTIMATE MECHANICAL PROPERTIES OF THERMALLY EXPOSED BASALT FILAMENT YARNS

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Basalt fibers similarly as glass fibers can be used for production of high temperature resistant and chemically inactive products. The main problems of basalt fibers preparations is great unevenness due to gradual crystallization of some structural parts (plagioclase, magnetite, pyroxene) and due to non-homogeneity of melt [1]. Utilization of the technology of continuous spinning overcomes the problems with unevenness and resulted filament yarns are applicable in the textile branch. It is possible to use these yarns for production of planar or 3D textile structures for composites, special knitted fabrics and also as the sewing threads. Especially an application of basalt yarns as the sewing threads is very attractive. It is possible to use these threads for joining of filtering bags for hot media, filtering bags for very aggressive chemical environment, etc. [3]

The fresh basalt fibers are practically amorphous. Due to high temperature action these fibers have ability to partially crystallize. This modified form of basalt fibers can be more brittle and the strength can be too low. In this contribution the strength of basalt filament yarns are investigated at room temperature and after tempering to the 50, 100, 200, 300 °C. Structural changes of fibers are identified by scanning electron microscopy. The strength drop of basalt filaments after long term temperature exposition is described by the linear spline nonparametric model.

BASALT FIBERS

Basalt is generic name for solidified lava which poured out the volcanoes [1, 2, 5,6]. Basaltoid rocks are melted approximately in the range 1500 - 1700°C. When this melt is quickly quenched, it solidified to glass like nearly amorphous solid. Slow cooling leads to more or less complete crystallization, to an assembly of minerals. Two essential minerals plagioclase and pyroxene make up perhaps 80% of many basalts. Classification of basaltoid rocks based on the contents of main basic minerals is described in the book [5]. Basaltoid rocks which are suitable for creation of fibers contain often green mineral Olivine

($2(\text{MgFe})\cdot\text{O}\cdot\text{SiO}_2$) and Nepheline ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$). From the point of view of chemical composition of basalts the silicon oxide SiO_2 (optimal range 43.3 - 47%)

dominates and Al_2O_3 (optimal range 11 - 13%) is next in abundance. Content of CaO (optimal range 10 - 12%) and MgO (optimal range 8 - 11%) is closely similar. Other oxides are almost always below 5% level. The color of basalt is from brown to the dull green in dependence on the ferrous oxides content. In the practice the suitability of basaltoid rocks for fibers preparation is based on their chemical and mineralogical composition. Attention should be also paid to the textural characteristic of the respective rocks [7].

Basalts are more stable in strong alkalis than glasses. Stability in strong acids is slightly lower. Basalt products can be used from very low temperatures (about -200°C) up to the comparative high temperatures $700 - 800^\circ\text{C}$. At higher temperatures the structural changes occur.

Basalt rocks from VESTANY hill were used as a raw material in this work. Based on the DTA measurements the crystallization temperatures T_c of individual minerals are evaluated. For Magnetite $T_c = 720^\circ\text{C}$ for Pyroxene $T_c = 830^\circ\text{C}$ and for Plagioclase $T_c = 1010^\circ\text{C}$.

The filament yarn contained 280 single filaments and was used for investigation.

STRENGTH OF BASALT AFTER THE THERMAL EXPOSITION

Behavior of basalt filament yarns after long-term thermal exposition was simulated by tempering of fibers at the temperatures $50, 100, 200, 300^\circ\text{C}$. The time of exposition was 60 min. After the tempering the tensile strength $[\text{N.tex}^{-1}]$ was measured on the TIRATEST 2300 machine. It was determined, that only 300°C tempering led to statistically significant drop of strength. Probably, these changes are a result of the changes of crystalline structure of fibers.

In the second set of experiments the strength distribution of basalt filament roving was measured on the samples tempered in oven at temperatures $T_T = 20, 50, 100, 200, 300, 400$ and 500°C in time intervals $t_T = 1, 15$, and 60 min. The 50 samples of strengths P_i are collected. These values were recalculated to stress at break values σ_i $[\text{GPa}]$. The strength distribution of tempered filament yarns was nearly Gaussian with parameters: mean σ_p and variance s^2 [8-12]. These parameters are estimated by the sample arithmetic mean σ_p and sample variance s^2 . Results are given in the table I.

Table I. Parameters of Tempered Roving Strength

t_T [min]	1		15		60	
T_T $[\text{C}]$	σ_p $[\text{GPa}]$	s^2 $[\text{GPa}^2]$	σ_p $[\text{GPa}]$	s^2 $[\text{GPa}^2]$	σ_p $[\text{GPa}]$	s^2 $[\text{GPa}^2]$
20	1.01	.0075	1.01	.0075	1.01	.0075
50	.997	.0110	1.05	.0110	1.07	.0150
100	1.03	.0095	.991	.0140	1.01	.0100
200	.986	.0091	1.01	.0083	1.09	.0110
300	.893	.0140	.743	.0150	.424	.0100
400	.743	.0061	.701	.0091	.112	.0015
500	.254	.0048	.348	.0026	.0940	.0030

The dependence of the roving strength on the temperature exhibits two nearly linear regions. One at low temperature to the 180°C with nearly constant strength and one up to the 340°C with very fast strength drop. For description of this dependence the linear spline model has been used [11]. By the linear least squares the strengths σ_1 for temperature $T_1=180^\circ\text{C}$ and σ_2 for temperature $T_2=340^\circ\text{C}$ were computed. These values and the rate of strength drop $D = (\sigma_1 - \sigma_2) / 160$ [GPa deg⁻¹] are given in table 2.

Table 2. Thermal Dependence of Roving Strength

t_T [min]	σ_1 [GPa]	σ_2 [GPa]	D [GPa deg ⁻¹]
1	1.0074	.756	.0016
15	1.1070	.343	.0048
30	1.1750	.158	.0064

CONCLUSION

From thermal dependence of the filament yarns strength is evident that long term exposition at temperatures above 200°C leads to the drop of mechanical properties probably due to gradual crystallization. This hypothesis was verified by the electron microscopy of fibers break zone.

ACKNOWLEDGEMENTS: This work was supported by the Czech National Grant Agency (grant No. 106/97/0372)

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FLAME RETARDANT EFFECTS OF MAGNESIUM HYDROXIDE WITH INTUMESCENCE ADDITIVES FOR POLYPROPYLENE

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Nowadays, more and more frequently halogen-free fire retardants are used for the reduction of polyolefin flammability. Hard-to-ignite polypropylene can be obtained by the introduction of a large quantity of mineral fillers (such as alumina trihydrate, magnesium hydroxide and basic magnesium carbonate) which lose water during their thermal decomposition. The mechanism of fire-retarding action of these compounds consists mainly in condensed phase temperature reduction as a result of endothermic decomposition accompanied by the evolution of water which additionally dilutes polymer decomposition products. In order to increase the amount of fillers introduced to polyolefins, the fillers are frequently modified by the addition of polyfunctional silane monomers which improve the dispersion of a filler. Magnesium hydroxide is very efficient in limiting smoke emission from burning plastics, first of all due to the removal of heat from a plastic during its decomposition. Products of decomposition form a barrier around the plastic and bring about the formation of carbonaceous layer which retards the evolution of potentially combustible gases. Unfortunately, the large contribution (about 30%) of the fillers to the composition of modified plastic materials affect, as a rule, processing and physico-mechanical properties of the composite materials.

Very effective fire-retardants for thermoplastics appeared to be so-called intumescent systems which give them fireproofing properties by the formation of carbonaceous foam having a large volume and protecting underlying material from further action of flames. The awareness of high hazard associated with the generation of large quantities of dense smoke and toxic or corrosive substances formed as a result of combustion (this hazard accompanies, as a rule, fire-retardant systems based on mixtures of halogenated compounds and metal oxides) has a stimulating effect on the studies of exploiting fire-retarding potential of intumescent systems added to polymers such as polyolefins. However, the incorporation of an intumescent component into polymeric material is associated with several problems. First of all, the additives have to be thermally stable at polymer processing temperature and have to be compatible with polymer matrix in order to obtain good dispersion and low solubility in water to avoid hygroscopicity of polymeric material. The addition of intumescent substances to polypropylene brings about the formation of insulating foam during heating and this, in turn, retards the decomposition of

plastic present under the foam layer as well as prevents from the evolution of toxic and combustible gases to a significant extent. Three components are necessary to achieve satisfactory action of intumescent systems:

- carbon-forming compound, e.g. polyhydric alcohol,
- esterification catalyst, e.g. ammonium polyphosphate,
- pore-forming agent, e.g. organonitrogen compound.

On the other hand it is well-known that the addition of inorganic fillers like magnesium compounds to polypropylene can cause changes in the structure and properties of the composite resulted. Mechanical properties of the product depend on the adhesion energy between inorganic component and polymer matrix and on the structure of polypropylene matrix.

In this work we present results of our study on flammability of polypropylene samples containing various fire retardants. Moreover, the influence of the flame retardants added to PP on the structure of polypropylene matrix was investigated.

The effect of magnesium hydroxide on thermal properties of isotactic polypropylene was measured on a cone calorimeter. The measurements were performed in air at heat flux of 50kW/m^2 .

The influence of different kinds and quantities of $\text{Mg}(\text{OH})_2$ on fire properties of isotactic polypropylene-containing composites was studied using the systems as follows:

- polypropylene + magnesium hydroxide (20, 30, 35 and 40 wt % of MagShield S, MagShield M-SE, MagShield M-SA, MagShield M),
- polypropylene + 30 wt % of the following mixtures of MagShield with intumescent compounds:
 - MagShield S (1 part by weight) – pentaerythritol (1 part by weight) - urea polyphosphate (3 parts by weight)
 - MagShield S (1 part by weight) – pentaerythritol (1 part by weight) - melamine polyphosphate (3 parts by weight)
 - MagShield S (2 parts by weight) – pentaerythritol (0.5 part by weight) - zinc borate (2 parts by weight) .

MagShield has a beneficial effect on polypropylene combustion parameters. Its addition results in the decrease in heat release rate, mass loss rate, total heat of combustion and effective heat of combustion. The optimum amount of MagShield is about 30%.

Melamine polyphosphate, when added to MagShield-PP system, shows the highest fire-retarding effect compared to other intumescent compounds studied, such as pentaerythritol, urea polyphosphate and zinc borate. The weakest effect was recorded for zinc borate-containing composite.

Results of the structural study allow to conclude that fire retardants based on magnesium compounds in practice do not change the crystalline structure of isotactic polypropylene.

The intumescent fire retardants act as nucleants of hexagonal form of isotactic polypropylene.

ACID -BASE CHARACTERISTICS OF THE SURFACE OF UV-CURABLE URETHANEACRYLATE PROTECTIVE COATINGS OF OPTICAL FIBRES

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The optical fibres may be considered as a composite materials composed of two parts, greatly different in their physicochemical properties: glass inner part and the outer one, prepared from UV-cured polymers. Thus, the mechanical strength of the optical fibre depends not only on the mechanical properties of its two parts but also on the adhesion of polymer protective coating to the glass surface. It was demonstrated that high adhesion of polymer protective coating leads to an increase of the mechanical strength of optical fibres[1].

According to the Fowkes approach [2] the adhesion energy W_a consists of two terms resulting from the dispersion interaction W^{LW} and the donor-acceptor interaction W^{AB} of both surfaces being in contact. In the case of the system composed of a solid wetted by a liquid the adhesion energy (or a interfacial free energy) can be determined using the Yung's equation

$$W_a = \gamma_L(1 + \cos\Theta)$$

where γ_L is the surface tension of a liquid and Θ is the contact angle of a liquid on the solid surface. The problem of adhesion between the surfaces of two solids (e.g. optical fibre and its protective coating) is much more complicated. However, according to van Oss approach [3] it is possible to determine the surface free energy γ_s of a solid and its electron donor and electron acceptor components using the contact angles of three different liquids for which these components are known. The following equation describes the dependence of the surface free energy on the contact angle and the donor-acceptor components of the liquid surface tension:

$$(1 + \cos\Theta)\gamma_L = 2(\gamma_s^{LW}\gamma_L^{LW})^{1/2} + 2(\gamma_s^+\gamma_L^-)^{1/2} + 2(\gamma_s^-\gamma_L^+)^{1/2}$$

where γ_L^{LW} , γ_L^+ and γ_L^- are the dispersion, electron acceptor and electron donor components of the liquid surface tension and γ_s^{LW} , γ_s^+ and γ_s^- are the same components of the surface

free energy of the solid. The dispersion interactions are symmetric but the specific ones can occur only when one of the contacting surface is electron donor and the other one is electron acceptor. Thus using three liquids (usually water, formamide and diiodomethane) to measure the contact angles on the solid surface and solving three equations of given type it is possible to calculate the components of its surface energy. The knowledge of them allows to predict if the adhesion between the optical fibre surface and the polymer protective coating will be the result of only dispersion or will be stronger due to specific interaction.

In our previous works [4,5] we have shown the method of measurement of adhesion energy of UV-curable epoxyacrylate polymer protective coating of as well as the surface characteristics of fused silica and these polymers. In this paper we will present the surface properties of the new group of UV-curable urethaneacrylates used as the protective coatings of optical fibres. Using the van Oss as well as the inverse gas chromatography methods we have shown that the surface of polymers investigated has an electron-donor character. Also, the influence of the kind of active diluent of the surface properties of cured polymers will be demonstrated.

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LUMINESCENT MATERIALS BASED ON THE ANTENNA EFFECT IN XEROGELS

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The sol-gel method has been shown as a suitable approach for the preparation of novel luminescent materials. On the other hand, there is a great interest to modify the coordination environment of Eu^{3+} ion to improve their absorption characteristics and to reduce non-radiative decay mechanism from the excited state [1]. In this case cage-like ligands (cryptands) have been designed. They are capable of encapsulating the metal ion. Of special interest are the cryptates with lanthanide ions where energy transfer from the cryptand to the central ion takes place [2]. This type of play an antenna role. One of the cryptand ligands is the 3,3'-biisoquinoline-2,2'-dioxide (indicated here as *biqO₂*). In order to remove water and OH groups from the coordination sphere and to isolate the central ion from these quenchers the Eu(III) cryptate were additionally complexed with secondary ligands such as 1,10-phenanthroline (*phen*) or triphenylphosphin oxide (*TPPO*).

One of the major advantages of the sol-gel process is the possibility of preparing multicomponent systems at low temperature. The sol-gel techniques can be used for the synthesis of organically modified silicates (ORMOSILs) which represent hybrid systems consist of both inorganic oxide network and methyl groups [3,4]. Europium(III) complex with *biqO₂* and complexes with additional, secondary ligands such as: *phen* or *TPPO* were entrapped by the sol-gel method in silica or silicate xerogel organically modified with methyl groups. The luminescence behaviour of the complexes in the rigid matrix was studied by means of emission, excitation spectra and lifetimes. The result indicated that the Eu(III)-*biqO₂* complex in the methylated silicate xerogel showed distinctly higher emission intensity and longer lifetime than in the silica matrix. It was also observed for the silica xerogel with Eu(III) complex that emission intensity increased up to 110 °C with increasing temperature.

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SAXS INVESTIGATION OF AMINOLIZED TMPA/BA COPOLYMER AND TMPA/BA/VA TERPOLYMER

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The samples of the: TMPA, TMPA/BA and TMPA/BA/VA polymers were obtained using the Suspension polymerisation method [1]; the monomers were diluted with a mixture 9:1 (v/v) of Qykiohexanol and ²-ethylhexanol with the volume ratio of the dilutes to the monomers v_d/v_m :1:1 (A series) or 2:1 (B series). The polymers were aminolysed with ethylenediarnine for; 2, 4, or 5 hours for the preparation of the reactive hydrogels. The SAXS measurements were made on the compact Erailcy camera (A-PAAR) equipped with the HECUS-MBRAUN optical system, using Cu target X-ray tube as the radiation source ($\lambda = 1.542 \text{ \AA}$).

For the each sample examined of both polymers and related to them hydrogels the a_1 short and a_2 long correlation distance [2-4], the α scattering exponent and the fractal dimension: D_m , D_p and/or D_a [5] were deterrni~ed direct~y from the smeared SAXS curves after the background subtraction (the background was subtracted in accordance with Ruland background equation) [7]. The thickness of the interphase boundary was estimated in relative units, by the new proposed parameter d_{eff} (boundary diffusions). The parameter my be defined basing on the P.W. Schmidt concept of the fuzzy pore boundary [7, 8].

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Table I. Results of SAXS investigations of aminolized TMPA/BA copolymer and TMPA/BA/VA terpolymer
($h=4\pi \sin \theta/\lambda$ - the scattering vector; $\lambda=1.542$ [Å])

SAMPLE	Description	Range of: h [Å ⁻¹] & $1/ha$ [Å]	α scatter. exponent	Suggested fractal type & determined fractal dimension	Range of h [Å ⁻¹] & $1/ha$ [Å]	α scatter. exponent	Suggested fractal type & determined fractal dimension	α scatter. exponent for Porod range	β ($\alpha-4$)/2	d_{eff} diffuseness of phase boundary (new proposed parameter: $d_{eff}=0.9^{1/\beta}$)
BE*TMPA/BA very small porosity [6]	aminolized copolymer for 5h	0.011-0.063 92-16	3.49	surface fractal $D_s = 2.4$	0.079-0.25 13-4	2.67	porous fractal $D_p = 2.7$	-	-	-
BE VA3 very small porosity [6]	aminolized terpolymer for 2h	0.011-0.028 92-35.7	3.53	surface fractal $D_s = 2.5$	0.031-0.079 32-12	2.83	porous fractal $D_p = 2.8$	4.6	0.3	0.7
BE*VA2 very small porosity [6]	aminolized terpolymer for 2h	0.011-0.04 92-25	3.48	surface fractal $D_s = 2.4$	0.045-0.113 22-9	2.65	porous fractal $D_p = 2.7$	5.0	0.5	0.8
BE*VA2 very high porosity [6]	aminolized terpolymer for 5h	0.011-0.028 92-36	3.49	surface fractal $D_s = 2.5$	0.036-0.1 28-10	2.31	mass fractal $D_s = 2.3$	4.0	0	0
AE VA1 very small porosity [6]	aminolized terpolymer for 4h	0.011-0.2 92-5	3.32	surface fractal $D_s = 2.7$	-	-	-	-	-	-
AE VA2 very small porosity [6]	aminolized terpolymer for 4h	0.011-2 92-5	3.30	surface fractal $D_s = 2.7$	-	-	-	-	-	-

Biocomposites and Biomimicry

Invited lecture**POLYMERIC ENZYME MIMICS****Man Jung Han and Kyung Soo Yoo**Department of Applied Chemistry, Ajou University
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Synthesis and activity tests of the enzyme models and mimics drew much attention for the elucidation of the enzyme structures and mechanisms. The cyclodextrinyl compounds capped with imidazole rings showed catalytic activities for the hydrolysis of phosphodiester¹⁻³ and the ribose-containing polymers catalyzed the cleavage of DNA.^{4,5} We have synthesized the cyclodextrinyl compounds capped with ribose and the polymers containing ribose rings, and tested their activities for the model reactions of nuclease, ligase, phosphatase, and phosphorylase, and for the cleavage of nucleic acids.

The reaction of 6-monotosyl- β -cyclodextrin with 5-amino-5-deoxy-1,2-O-isopropylidene- α -D-ribose gave 5-(β -cyclodextrinylamino)-5-deoxy-1,2-isopropylidene- α -D-ribose, which was hydrolyzed to result in 5-(β -cyclodextrinylamino)-5-deoxy- α -D-ribose. The latter compound catalyzed hydrolysis of phosphodiester (nuclease), the esterification of phosphomonoester to phosphodiester (ligase), the hydrolysis of phosphomonoester (phosphatase), and the phosphorylation of alcohols with phosphate ions (phosphorylase).

Poly(5-acrylamido-5-deoxy- α -D-ribose) was synthesized by polymerization of 5-acrylamido-5-deoxy- α -D-ribose with the aid of radical initiator (AIBN). The polymer showed also catalytic activities for the model reactions of nuclease, ligase, phosphatase, and phosphorylase as mentioned above. The polymer catalyzed the cleavage of nucleic acids (DNA and RNA).

The study of model reactions with cyclodextrinyl compound showed clearly that the *vic-cis*-diol of the ribose ring capped on the cyclodextrin formed hydrogen bonds with the two phosphoryl oxygen atoms of the phosphate so as to activate the phosphorus atom to be attacked by nucleophiles, water or alcohol. The polymer containing ribose rings formed active sites by chain folding. The ribose rings having *vic-cis*-diol groups were located inside of the active sites, where the phosphodiester substrates were also accommodated. The polymer showed the catalytic activities by the similar mechanisms of the model compound.

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Invited lecture

**ADVERSE BIOLOGIC RESPONSES TO POLYMERS, METALS
AND OTHER PROSTHETIC MATERIALS**

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In recent years, the alleviation of bodily structural and functional defects has been greatly facilitated with innovative exogenous materials. Chief representation has been from families of polymers, metals and ceramics in an everwidening array of devices that have repaired or replaced faulty structures most notably in the cardiovascular, osseoskeletal and ocular tissues. Bioengineering efforts now flourish and endeavor to ameliorate dysfunction in virtually every tissue of the human or animal host.

A retrospective review of adverse effects of some of the applications of a half century of implants into the human body serves as a means of anticipating the needs of this rapidly expanding discipline. This brief overview of the uses of polymers and composites in the repair or replacement of tissues and organs summarizes many of the salient features of implant failure or deficiency. The ability to minuterize devices and processes has focused on vessel wall support, repair of cochlear function, perception of sight, smell and taste and nerve conduction among others. On a grander scale, replacement of functional extremities featuring ionic polymer metal composite "muscles" with both force and sensor capability is in test phase. Either as permanent inserts or as a temporary scaffold to support living grafts implants will continue to play a more expanding role in the bionic future of man.

Adverse reactions to implanted materials take on various forms ranging from implant failure to reactive processes with local or systemic implications. Locally, breakdown of implant components can lead to instability and failure. The latter may lead to fracture or fragmentation, the latter as particulate disease. Leaching of metals or other components may lead to toxic or allergic effects. The latter also encompasses so called adjuvant disease with systemic autoimmune manifestations. Intraluminal devices may obstruct with blood clot or accretions of crystalline or proteinaceous debris. The regional host milieu may undergo excessive scarring, hemorrhage, infection or tumoral development. Fragmented particles or blood clot can migrate to remote organs and lead to severe impairment of function or death. The introduction of newer modalities of substances into future devices will provide ever-increasing challenges to the scientific community to assure safety and prolonged applicability. Introduction of composites has potential for improved performance

reaching for lifetime integrity as well as incorporating factors that influence the healing phase favorably.

The consequences of untoward reactions have led to grave legal consequences, some of catastrophic proportions.

*Invited lecture***HYDROGELS SYNTHESIZED BY MEANS OF RADIATION
TECHNIQUE AND THEIR MEDICAL APPLICATIONS****Janusz M. Rosiak**Institute of Applied Radiation Chemistry, Technical University of Łódź
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Medical advances that have prolonged the average life span have generated increased need for new materials that can be used as tissue and organ replacements, drug delivery systems and components of devices related to therapy and diagnosis. The first man-made plastic used as surgical implant was celluloid, applied for cranial defect repair. However, the first users applied commercial materials with no regards for their purity, biostability and postoperative interaction with the organism. Thus, these materials evoked a strong tissue reaction and were unacceptable. The first polymer which gained acceptance for synthetic materials was poly(methyl methacrylate). But the first polymer of choice, precursor of the broad class of materials named today as hydrogels, was poly(hydroxyethyl methacrylate) synthesized in the fifties by Wichterle and Lim. HEMA and its various combinations with other polymers, both hydrophilic and hydrophobic, are till now the most often used hydrogels for medical purposes.

Hydrogels are two- or multicomponent systems consisting of a three-dimensional network of polymer chains and water that fills the space between macromolecules. Depending on the properties of the polymers used, as well as on the nature and density of the network joints, such structures in an equilibrium can contain various amounts of water; typically in the swollen state the mass fraction of water in a hydrogel is much higher than the mass fraction of polymer. Two general classes of hydrogels can be defined - physical gels or pseudogels, where the chains are connected by electrostatic forces, hydrogen bonds or chain entanglements (such gels are non-permanent and usually they can be converted to polymer solutions by heating) and chemical (true, permanent) hydrogels with covalent bonds linking the chains.

Although many applications of hydrogels may be listed, perhaps the most promising and sophisticated is their use in the field of medicine and pharmacy. Over 30 years of research in this field resulted in the common use of hydrogels as soft contact lenses, wound dressings, drug-delivery systems, superabsorbents, *etc.*, with a number of products being commercially available.

Nowadays a new class of hydrogels, capable of reacting to various environmental stimuli as temperature, pH, ionic strength, solute concentration, electric field, light, sound, *etc.*, is tested for use in the so-called "intelligent biomaterials". Certainly there is still a big gap between the artificial hydrogel fish that moves by swinging its tail in a laboratory bath and

an implementation of artificial muscles. However, rapid progress in this field, correlated with increasing demands for more effective medical treatment indicates that there is no exaggeration in including these systems in the list of the "materials of XXI century".

Ionizing radiation has been since long recognized as a very suitable tool for the formation of hydrogels. Easy process control, possibility of joining hydrogel formation and sterilization in one technological step, no necessity to add any initiators, crosslinkers, *etc.*, possibly harmful and difficult to remove, no waste, relatively low running costs - this makes irradiation the method of choice in the synthesis of hydrogels, especially for biomedical use although, certainly, this technique has also some limitations and not every kind of hydrogel we may think of can be synthesized in this way. Also from the point of view of radiation chemistry, crosslinking of polymers, including hydrogel formation, belongs to the most successful applications of this branch of science.

Design and optimization of efficient, safe and economically sound radiation-based technologies of hydrogel formation requires the knowledge of the underlying radiation chemistry. This need has been since long one of the main factors stimulating the investigations on radiolysis of polymers in aqueous solutions.

Another important reason to undertake such studies is the potential application of their results in the understanding of the radiation-induced effects in more complicated polymeric systems, namely biopolymers such as DNA, polysaccharides and proteins, *i.e.* problems that are of primary importance for radiation biology.

In this lecture some directions of investigations on the radiation formation of hydrogels have been briefly discussed, focusing on the problems studied by our Group in the recent years. Also, some examples of commercialized products being produced by means of radiation technique have been presented.

Invited lecture

SYNTHESIS AND CHARACTERIZATION OF OLIGOPEPTIDES AS A NEW ORAL DRUG DELIVERY SYSTEM

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In the last two decades, efforts have been made to develop effective delivery systems for potential therapeutic peptides and protein drugs. Recent progress in recombinant technology for producing peptides and proteins for pharmaceutical use further promoted the need for the development of new delivery systems.

In 1990, Steiner and Rosen (U.S. Patent 4925673) reported that proteinoid materials are effective for oral delivery of peptides and proteins, such as insulin and α -interferon. The proteinoid materials were generated by the thermal condensation of amino acid mixtures. The proteinoid materials obtained form microspheres with drugs in a pH-dependent manner, i.e.; the microspheres are stable at a low pH and disassemble near neutral pH. This mechanism effectively protects the biologically liable peptides and proteins from the acidic pH (pH 1~2) and digestive enzymes in the stomach, while the microspheres disassemble in the intestine region (pH 6~7) releasing the drug. In addition to the ability to provide these protective effects, the proteinoid materials appear to facilitate the absorption of macromolecular drugs from the intestine. This drug absorption mechanism seems unique compared to other polymeric microsphere delivery systems.

The precise mechanism of proteinoid oral drug delivery system is still unclear. This led us to explore the proteinoid oral delivery system using the structurally define oligopeptides. We synthesized a series of acid oligopeptides and evaluated their physicochemical properties and sphere formation behavior. The purpose of this study is to obtain basic information about the drug absorption mechanism of proteinoid oral drug delivery system using the oligopeptides. Heparin and insulin were used as carbohydrate and protein model drugs, respectively, since the proteinoid materials facilitated oral delivery of both of these agents. The interaction between the oligopeptides and these drugs after the microspheres disassemble at neutral pH (pH 7.4) was investigated by fluorescence and circular dichroism (CD) spectroscopy and isothermal titration calorimetry (ITC).

Invited lecture**SYNTHESIS OF BIOMIMETIC PHB AND ITS POTENTIAL UTILITY
IN MEDICAL APPLICATIONS****Zbigniew Jedliński**Polish Academy of Sciences, Centre of Polymer Chemistry
34, Maria Curie-Skłodowska Str., 41-819 Zabrze, Poland

In an attempt to synthesize poly-(*R*)-hydroxybutanoic acid similar to natural PHB present in living systems, we have employed anionic initiators in the polymerization of β -butyrolactone.

The yield of the ring-opening reaction of β -butyrolactone could be enhanced only if a crown ether, e.g. 18-crown-6, was added to the potassium alkoxide used as an initiator and the activation of alkoxide anion occurred due to complexation of potassium cation. It turned out that polymerization proceeds regioselectively with the inversion of configuration due to a substitution-elimination mechanism operating in this reaction. Thus polymers with *R* configuration of the polymer chains could be synthesized if the *S*-monomer was used as a substrate. However, due to the substitution-elimination mechanism, the polymer chains also contain a certain number of unsaturated crotonate end groups as confirmed by ESI-MS analysis. Thus the structure of synthetic polymers is similar but not identical with the native natural PHB polyesters.

Therefore, the ability of the sodium salt of (*R*)-3-hydroxybutanoic acid activated by a crown ether to function as an initiator was examined. The experimental results showed that the polymerization of (*S*)- β -butyrolactone with this initiator, performed in the bulk phase or in an organic solvent, proceeds regioselectively with the inversion of configuration, yielding poly-(*R*)-3-hydroxybutanoic acid exhibiting the same stereochemistry and end groups as present in natural PHB.

The molecular weight of the resulting linear polymers depends on the monomer-to-initiator molar ratio. The molecular weight distribution is relatively narrow ($M_w/M_n = 1.1-1.2$), which is indicative of the uniformity of polymers obtained. As evidenced by ^1H NMR spectroscopy the synthetic biopolymers are entirely isotactic and crystalline.

Studies on the biocompatibility of this synthetic PHB are under way.

Invited lecture

**POLYGLICOLIDE/LACTIDES/CAPROLACTONE HOMO
AND COPOLYMERS FOR SOME SELECTED USE IN MEDICINE**

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Polyglycolide/lactate/caprolactone homo and copolymers with different molecular weights and chain structures were prepared by direct polycondensation and/or by ring-opening polymerization of the respective monomers and dimers in bulk by using Sb_2O_3 or stannous octoate as the initiator, respectively. Polymers were characterized by FTIR, NMR, GPC, DSC, etc. Copolymers of polylactides with polyethylene oxides by transesterification were also synthesized. Polymeric particles carrying drugs were produced by a solvent evaporation procedure. Fibers were prepared both dry and melt spinning and drawing. Non woven matrices were produced by a winding process. Membranes were solvent-casted from the proper solutions. Copolymers of D,L-lactate and ϵ -caprolactone were gummy and were mixed with hydroxyapatite to prepare composites. Poly(L-lactate) with high molecular weights with or without hydroxyapatite were processed into pins by compression moulding. All these materials were tested in animal models, as drug delivery systems, sutures, wound dressings, soft and hard tissue filling materials and repair. This presentation overviews

Invited lecture

**CHARACTERIZATION AND PROPERTIES
OF NEW HAEMOCOMPATIBLE MATERIALS
WITH A BASIS OF HYALURONIC ACID**

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The utilisation of polysaccharides in medicine is well known and widespread. A great deal of diverse chemistry has been applied and many new hydrogels have been described in the literature expanding more and more their therapeutic application. Notwithstanding these intense studies, there are in the literature a very few examples of hydrogels with well characterised functional linkers. Here a new approach for the synthesis of polysaccharide hydrogels has been performed, in which the variation of polysaccharide/crosslinking agent ratio together with the type of cross-linker as well the chemical nature of the polysaccharide is the effective route to altering gel properties.

Polyurethane having bound sulfated hyaluronic acid was synthesized through two different chemical routes. Both the materials obtained consist of a hydrophilic component sulfated hyaluronic acid (HyalS_{3,5}) and a hydrophobic component polyurethane (PU).

The bacterial adhesion and the *in vitro* haemocompatibility of a material based on polyurethane and poly(amido-amine) (PUPA) was also evaluated both in its native form and with anticoagulant molecules such as Unfractionated Heparin (U.H.) and sulphated hyaluronic acid (HyalS_{3,5}) electrostatically bonded to its surface.

Invited lecture

**SURFACE CHEMISTRY OF BIOMATERIALS:
DESIGN OF POLYMER SURFACE PROPERTIES FOR TISSUE
ENGINEERING AND WOUND HEALING APPLICATIONS**

Joseph A. Gardella, Jr., Jiaxing Chen, Joo Woon Lee, Denise E. Carney

Department of Chemistry and Center for Advanced Photonic and Electronic Materials

Wesley Hicks, Jr.

Department of Surgery, Roswell Park Memorial Cancer Institute
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This paper will review new approaches to the determination of the reaction kinetics of biodegradation of polymers used in scaffolding and drug delivery applications. A new technique based on Time of Flight Secondary Ion Mass Spectrometry can be used to screen polymers and their preparations for their degradation properties. We have used this method to evaluate new materials and preparations of materials for the delivery of growth factors to control epithelial proliferation and growth and suppression of fibroblast scar tissue growth in designing a synthetic biodegradable membrane for tracheal wound healing.

Results from the new methods and new materials, including the relationships between polymer surface properties and cell adhesion and growth will be presented.

Invited lecture

**THE WORLD'S SMALLEST DEVICES? NANOOPTOCHEMICAL
SENSORS FOR BIOMEDICAL APPLICATIONS**

**Raoul Kopelman, Heather Clark, Murphy Brasuel, Michael Miller, Zoe Chen,
John Aylott, Serban Peteu, Hao Xu, Steve Parus, Marion Hoyer*
and Martin Philbert***

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Optochemical sensors with radii as small as 10 nm have been developed for real-time biochemical analysis in sub-cellular environments. They are based on fluorescent probes embedded in polymeric matrices or glasses, often in conjunction with ionophores, sensitizers, stabilizers or enzymes. Also, dendrimeric photoantenna supermolecules have been designed and tested for increased quantum efficiency and photostability. These PEBBLE (Probe Encapsulated By Biologically Localized Embedding) sensors are inserted into a cell singly or in groups, depending on the delivery system (gene gun, picoinjector, liposome or ingestion). Good signal/noise and stability are combined with high spatial and temporal resolution and chemical detection. Compared to fluorescent molecular probes, these PEBBLEs are synergistic molecular devices, with a much wider range of chemical analytes, improved selectivities, higher precision and reduced chemical interferences. They have been successfully applied to viable human neuroblastoma, macrophage and other single mammalian cells. The simultaneous operation of a set of such sensors (each for a different analyte) results in real-time chemical analysis of primary physiological processes in the cell, under natural, pathogenic or therapeutic conditions.

Invited lecture

ACCELERATED MINERALIZATION OF PROSTHETIC HEART VALVES

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Industry/University Cooperative Research Center for Biosurfaces

This investigation demonstrated accelerated mineralization of glutaraldehyde-fixed bioprosthetic tissues at room temperature using a supersaturated solution of calcium-phosphate. Extensive mineralization of dynamically flexed pericardium samples was observed after 1 million cycles in a high speed valve tester at frequencies greater than 12 Hz. Mineralization of a dynamically tested porcine bioprosthetic heart valve was observed after 1 million cycles in pulse duplicator at physiologic pressures, flows, and rates. Unconstrained human umbilical cord vein grafts did not mineralize with respect to calcium and phosphorus after nearly 200 hours of exposure to the same solution. Internal stenting of these vessels, if it promotes mineralization under the same test conditions, will herald the introduction of a valuable new model for accelerated testing of new stenting concepts and materials.

Invited lecture**SYNTHESIS AND ANTITUMOR ACTIVITY
AND ANTIANGIOGENESIS EFFECTS OF PHTHALIC ACID
DERIVATIVE POLYMERS WITH MEDIUM-
MOLECULAR-WEIGHT****Sun-Mi Lee, Chang-Sik Ha, and Won Jei Cho**Dept. of Polymer Sci. & Eng., Pusan National University
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It has been reported that many polyanionic polymers exhibit good antitumor activities as well as toxic side effects. Some studies have been performed in our laboratory for several years.¹⁻⁴⁾ One of the methods for the reduction of cytotoxic side effects is to synthesize the medium molecular weight antitumor drugs which expected to have some advantages such as higher specificity of actions and longer duration of actions as compared with low molecular weight antitumor drugs.⁵⁻⁶⁾ Also, It has been reported that inhibition of angiogenesis might lead to control of tumor growth and metastasis.⁷⁾ Thus, treatment of angiogenesis inhibitors might be a novel strategy for tumor growth inhibition. The aim of present study was to synthesize new monomer and polymers with high antitumor and anti-angiogenesis activities against tumor cells and very low toxicity against normal cells.

The new monomer, α -alkoxy-*exo*-3,6-epoxy-1,2,3,6-tetrahydro-phthaloyl 5-fluorouracil was synthesized from 5-FU and α -alkoxy-*exo*-3,6-epoxy-1,2,3,6-tetrahydrophthaloyl chloride. Its homopolymer and copolymers with acrylic acid or vinyl acetate were prepared by the photopolymerizations at 25°C for 48 hr. The structures of the synthesized monomer and polymers were characterized by FT-IR, ¹H-NMR, ¹³C-NMR spectroscopies, and elemental analysis. The number average molecular weights of the synthesized polymers determined by GPC using DMF were in the range from 8,000 to 23,000. The *in vitro* antitumor activities and cytotoxicities of synthesized samples were evaluated against mouse mammary carcinoma, mouse leukemia, and human histiocytic lymphoma as cancer cell lines and mouse liver cell as a normal cell line. IC₅₀ values of synthesized samples were in the range of 0.03~35.21 μ g/ml against cancer cell lines. The cytotoxicities of synthesized polymers against normal cell line were lower than those of 5-FU. The *in vivo* antitumor activities of synthesized monomers and polymers were also investigated by Balb/C mice bearing the sarcoma 180 tumor cells. The antitumor activities of synthesized polymers were much greater than that of 5-FU. Synthesized samples were examined for anti-angiogenesis activities by using the chick embryo chorioallantoic membrane (CAM) assay.

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Invited lecture

THREE DIMENSIONAL FIBROUS SCAFFOLDS FOR TISSUE ENGINEERING

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INTRODUCTION

Fueled by the exciting progress made in biotechnology in recent years, Tissue Engineering is quickly becoming a method of choice for the development of implants in surgery. It is well known that biological tissues consist of well organized hierarchical fibrous structures ranging from nano to mm scale. (Fig. 1). The successful regeneration of biological tissue and organs calls for the development of fibrous structures with fiber architectures conducive to cell deposition and cell proliferation. Of particular interest in Tissue Engineering is the creation of reproducible and biocompatible 3-D scaffold for cell ingrowth resulting in bio-matrix composites for various tissues repair and replacement.

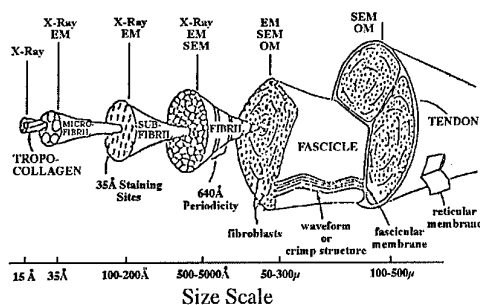


Fig. 1 (courtesy of Dr. Eric Baer)

HIERARCHICAL FIBER ARCHITECTURE DESIGN

There is a large family of fiber architectures available for surgical implants (Figure 2),[1]. The design and selection of these fiber architectures for tissue engineering can be carried out on the fiber level and structural level resulting in a wide range of dimensional scale, fiber tortuosity and fabric porosity as characterized by the fiber volume fraction-orientation map .

EXPERIMENTAL

To demonstrate our hierarchical design concept, experiments were carried out using osteoblasts isolated from neonatal rat calvaria and grown to confluence in Ham's F-12 medium (GIBCO), supplemented with 12% Sigma fetal bovine on PLAGA sintered spheres, 3-D braided 20 mm filament bundles and nanofibrils .Four matrices were fabricated for the cell culture experiments. These matrices include (1.) 150 - 300 mm PLAGA sintered spheres. (2.) Unidirectional bundles of 20 mm filaments (3.) 3-D braided structure consisting of 20 bundles of 20 mm filaments.(4.) Nonwoven consisting of nanofibrils. Cells were seeded on the UV sterilized PLAGA matrices at a density of 100,000 cells/sq. cm. The osteoblasts were cultured on the matrices for duration ranging

from one day to 21 days. They were prepared according to established procedures by fixing in glutaraldehyde and dehydrated through a series of ethanol dilution.

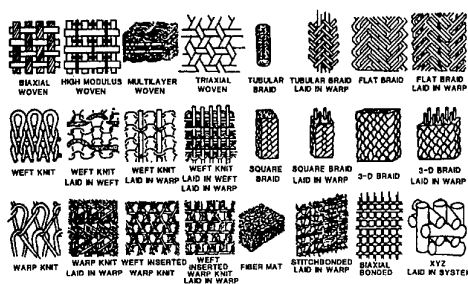


Fig. 2

Observations

Experimental results show that cell growth pattern is related to the relative dimensions between of the components in the scaffold and that of the cells. Scanning electron microscopy pictures were taken from the cell-matrix systems which were prepared in a series of Freon 113 dilution (25%, 50%, 75%, and 100%). The SEM samples were sputter coated with gold (Denton Desk-1 Sputter Coater). An Amray 3000 SEM using an accelerating voltage of 20

kV was employed to take the SEM photographs shown in Figures 3 to 5. It can be seen that , in responding to the large spheres wherein the cells are more than 10X smaller than the spheres, the cells tend to spread over the surface of the sphere before connecting to the adjacent spheres and eventually forming an interconnected cellular network. In the case of 20 mm filaments in unidirectional bundles and 3-D braided form wherein the cells are about the same order of magnitude in dimension, the cell-matrix reaction appear to be similar. The cells tend to slide off the matrix at the moment of seeding. Those cells remain on the surface of the substrates the cells tend to grow around the filaments and bridge onto the adjacent filaments along the length. The most intensive cell deposition was seen in the nanofibril nonwoven structure wherein the cells are more than an order of magnitude larger than the individual fibrils. Extensive cell spreading was observed along the length of the fibrils and through the thickness.

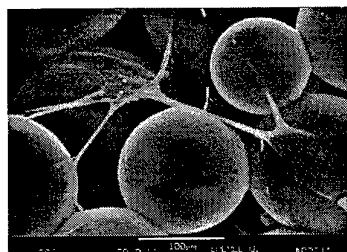


Fig. 3

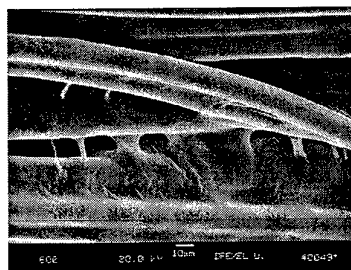


Fig. 4

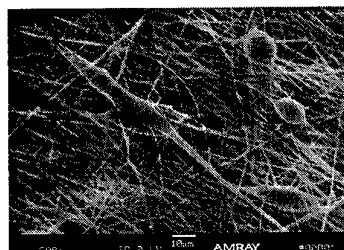


Fig. 5

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*Invited lecture***SILOXANE AND N-ACYLIMINOETHYLENE BASED
COPOLYMERS OBTAINED BY COMBINED POLYMER
SYNTHESIS TECHNIQUES**

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Polysiloxanes represent an unique class of polymers – they possess high hydrophobicity, good UV and oxygen stability, high chain flexibility, biocompatibility, but also weak mechanical properties and incompatibility with almost all organic polymers. To take advantage of their characteristics, they must be combined with chemically different polymeric sequences in block or graft copolymers to yield materials with new, interesting and promising properties and applications.

On the other hand, 2-oxazolines have been extensively investigated last years since their cationic ring opening polymerization, which presents a living character in appropriate conditions, is a convenient approach to the obtention of poly(N-acyliminoethylene) (PNAI) based polymeric materials. The interesting properties of PNAI (regular structure, high hydrophilicity and miscibility with organic polymers, biocompatibility, chemical versatility) give rise to various end uses – as nonionic polymeric surfactants, functional hydrogels, stabilizers for the preparation of monodisperse particles, compatibilizers, adhesives. However, in most cases such applications imply the combination of PNAI with other polymers, sometimes based on monomers polymerizable by different mechanisms.

The preparation of such block or graft copolymers (or more complex macromolecular architectures) requests strategies using combined polymer synthesis techniques. The presentation will focus on the synthesis, properties and applications of siloxane and N-acyliminoethylene based copolymers (the second sequence being mainly of vinyl type), as well as on block and/or graft copolymers with siloxane and N-acyliminoethylene sequences.

Invited lecture

TAILOR-MADE INTELLIGENT POLYMERS FOR MEDICAL APPLICATIONS

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Shape memory polymers are able to memorize a second, temporary shape besides their permanent shape. After application of an external stimulus, e.g. an increase in temperature, such a polymer can be transferred into its memorized shape. The process of programming and restoring a shape is reversible and can be repeated several times.

Shape memory alloys (e.g. CuZnAl, FeNiAl and TiNi-alloys) are being used in biomedicine as cardiovascular stents, guidewires and orthodontic wires. The shape memory effect of these materials is based on a martensitic phase transformation.

Biodegradable stimuli-sensitive polymers have a high potential in minimalinvasive medicine. Degradable implants can be brought into the body through a small incision in a compressed, temporary shape. When heating up at 37 °C, they will switch back to their memorized shape. A second surgery for removal of the implant is not required, since the new materials will degrade after a predetermined implantation time.

The shape memory effect is also existing for polymers. It is not a specific bulk property, but is resulting from the polymer's structure and morphology. The effect is persistent in many polymers, which might differ significantly in their chemical composition.

Some polymer systems having shape memory properties (thermoplastic elastomers and thermosets) will be introduced. Their thermal and mechanical properties as well as their degradation behavior will be discussed. Finally, first results about the biocompatibility of the new materials will be summarized.

Poster Session 1

P1.1.

**NATURAL FIBERS IN COMPOSITES. COMPARATIVE RESULTS
BETWEEN HEMP, KENAF AND FLAX FIBERS.
PREPARATION OF RAW MATERIAL AND FINAL PRODUCTS**

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Istituto Poligrafico e Zecca dello Stato, Roma - Italy

Biocomposites Centre, Bangor Gwynedd - UK

In the future, composite materials from natural fibers will have increasing importance in our life. They are light, recyclable, environment friendly. Natural fibers are asked to substitute the artificial fibers, which at present still perform better. Nevertheless, appropriate dry-mechanical treatment of raw material can help improving natural fiber characteristics; subsequent chemical treatments are able to induce fibers modifications that add to their resistance when utilized in composites products.

The will describe the hemp, flax and kenaf preparation system; results on yield and characteristics of different fraction will be given. Comparison will be made between the three species.

Afterwards, the composites preparation system will be described and results of fibers behavior in composites products will be illustrated and discussed.

Samples of raw material, pretreated fibers and composites will be presented.

P1.2.

FLAMMABILITY OF COMPOSITES BASED ON POLYPROPYLENE AND FLAX FIBERS

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Biodegradability and interesting physical and mechanical properties of polypropylene/cellulose composites are an essential motive for fundamental investigations on various properties of such materials [1, 2].

An addition of lignocellulosic particles to polymer results in a change in properties of the product obtained which is due to properties of lignocellulosic material and those of polymer depending on the proportion of both materials. It is also reflected in the flammability characteristics of the composites.

Our last paper presents interesting results obtained while studying isotactic polypropylene (PP) and composites based on PP with an admixture of flax fibers respectively 7.5% and 12.5%. The investigated plates were obtained from pellitized composite obtained through extrusion [3].

In this study we analyzed flammability of PP composites with long flax fibres, obtained by press method [4]. The amount of natural fibers was 12.5%, 20%, 30% and 40%. The thickness of investigated samples was 5 mm.

The samples were tested in accordance with ISO 5660 (Cone calorimeter) at heat flux of 35 kW/m². Heat release rate (HRR) and mass loss rate (MLR) curves show that thermal decomposition and combustion of the mentioned samples occur in a different way. In case of 12.5% flax fibers content HRR peak decrease of about 35% is observed. However, the time necessary for sustained ignition was in the cases of composites shorter than this for PP. The characteristic of the composite tends to be closer to that of lignocellulosic material. Even the addition of 12.5% fibers resulted in an increase in fire retardancy of composite compared to polypropylene alone.

The addition of fibres exceeding 20% made the composite materials characteristics resemble those of lignocellulosic materials.

ACKNOWLEDGMENTS

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P.1.3.

ACCELERATED DEGRADATION OF POLYMERS

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In recent years, there is a growing awareness caused by fast increase of plastic pollution. Recycling and incineration of plastic waste have many, serious limitations, thus, the production of new materials with enhanced degradation - plastics friendly for environment seems to be solution of this problem.

Application of photochemical processes for the environment protection against polymeric pollutants is discussed in this presentation. The main ways of acceleration of decomposition of high molecular compounds including the effect of UV-irradiation, metal salts, hydrogen peroxide and polymer blending are shown. The results of investigation of photo-oxidative degradation of selected commercial polymers using IR, UV-Vis spectroscopy, viscometry, gel permeation chromatography, optical microscopy and scanning electron microscopy are presented. The negative aspects of production of degradable polymers are also indicated.

P1.4.

NEW GENERATION COMPOSITE MATERIALS FOR SORPTION AND FILTRATION

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In recent years, the possibility of filtering air to remove various impurities has been greatly enhanced. The conventional filters fail to remove, from air, the molecules of irritant chemicals, odours, etc. And it is on the molecular level that pollution of air is the greatest. An average molecule is about ten thousand times smaller than the particles which can be removed by the conventional filters. Molecules can be removed by adsorption. One of the best adsorbents is activated carbon which effectively takes up molecules, from passing air, on its surface. Notable advances in filtration have been made by known Japanese, British, American [1-3], and Polish firms [4-5]

The American company Smart Filters, Inc., Colorado Springs, has developed a superior filter known as "Gray Matter" which is a combination of an electrostatic nonwoven fabric and activated carbon. The electrostatic fabric efficiently entraps the tiny particles and dust. The activated carbon adsorbs the odours and irritant molecules. The proportion of activated carbon in the filter is from 0.3% to 0.5%.

Also in Poland attempts have been made to develop new generation filters for the purposes of ventilation, air-conditioning, and protection of the respiratory duct. In a joint project, the Institute of Natural Fibres and VAMAG Werke GmbH have developed a process for surface combining of fine activated carbon granules with the fibres of a polyethylene nonwoven fabric. A special device has been constructed on which nonwoven fabrics of area weight from 125 to 250 g/m² can be 'powdered' with activated carbon of which the details are given in Table 1.

The activated carbon is bonded with the fibres by partial heat-sinking of its grains in the fibre surface. Carbon is deposited on the fibres in proportion to the area weight of the fabric, normally from 5% to 10%. The fabric with the deposited carbon is subjected to calendering, whereupon it made up into filter inserts.

The developed composite materials are capable of both sorption and filtration which notably extends the range of their application. For characteristics of the filters see Table 2. The sorption/filtration materials presented in Table 2 were subjected to laboratory and utility tests, and the following results were obtained:

1. Filtration efficiency – up to 99.5%;

Table 1. Properties of activated carbon SAR-P.

1	Methyl number	25 ml
2	Ash content	8.7%
3	Water content	3.8%
4	pH	6.8
	Grain-size 0.071 mm	12%
	distribution: 0.00 mm	88%

2. Filtration range – dust, molecules, odours;
3. Resistance to air flow – max. 200 Pa;
4. Filtration rate – $1.5 \text{ dm}^3/\text{s}$.

With filters of this type the effect of filtration is dependent on the structure and composition of the filter. The most important factors are: fineness of the fibres; type and grain-size of the activated carbon; packing density of the fibres; area weights of the components; and total area weight of the composite product. The presented composite filters were developed under a joint research project carried out by the Institute of Natural Fibres and VAMAG Werke GmbH on "Technology of Manufacturing New Generation Filter Materials for Protection of Health and Environment". As a result of the project new-generation world-standard filters have been produced for the first time in this country. Owing to their specific properties and construction, the filters can:

- a) entrap all solid particles by their nonwoven component;
- b) attract (by the electrostatic component) and entrap dust, allergenic pollen, spores of mould or fungi, bacteria and viruses;
- c) adsorb (on the activated carbon component) odours and molecules of irritant chemicals.

VAMAG Werke GmbH and Institute of Natural Fibres have applied to the Patent Office of Poland for a patent on the carbon depositing device and method of manufacturing the composite filters. VAMAG Werke GmbH is planning to start production of the new generation filters at a VAMAG factory in Poland (address: 42-240 Rudniki k/Częstochowy, ul. Stalowa 25, Poland).

Table 2. Characteristics of the composite sorption/filtration materials

	Type/structure	Weight (g/m^2)	Carbon (%)
1	One-layered, carbon-coated, calendered	125-250	10-5
2	Three-layered - inner layer – carbon-coated and calendered - outer layers - melt-blown	185-310 125-250 2x30	10-5
3	Three-layered - inner layer – carbon-coated and calendered - top layer – flame retardant - bottom layer – melt-blown	480 250 200 30	5
4	Three-layered - top layer – flame retardant - inner layer – carbon-coated and needled - bottom layer – melt-blown	430-630 200 200-400 30	4
5	Three-layered - top layer – electrostatic - inner layer – carbon-coated and needled - bottom layer – needled and calendered	550-750 200 200-400 150	4

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P1.5.

CORE YARNS WITH POLYMER ELASTANE CORE AND WOOL WRAPPING

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INTRODUCTION

The available elastane filaments are LYCRA® supplied by DuPont, DORLASTAN® supplied by Bayer, GLOSPAN® supplied by Globe (USA), LINEL® supplied by Fillattice, and others. They are all formed of a chain of synthetic polymers, containing a proportion of segmented polyurethane. The filaments vary in respect of their content of segmented polyurethane. For instance, in LYCRA® the content is at least 85%. These elastane filaments in a wrapping of a spun yarn or a filament yarn, e.g. a polyamide filament yarn, are used for the manufacture of hosiery or knitted sportswear. In the manufacture of woven apparel fabrics with elastic properties, among the yarns frequently used are worsted wool yarns twisted together with an elastane filament yarn in a wrapping of polyamide filament known as PAGASTIC. In the 1990's a method was developed by which elastane filaments with wrapping could be incorporated in a yarn directly in the ring spinning process. In the years 1997-98 a technology was developed at the Institute of Natural Fibres, Poznań, of manufacturing worsted wool core yarns with an elastane core, including LYCRA®, on ring spinning machines FIOMAX 2000.

TECHNOLOGICAL PROCESS AND RAW MATERIALS

The investigation in its technological part concerning the spinning of worsted core yarn with a LYCRA® core was carried out using a Süssen long-staple spinning frame FIOMAX 2000 provided with a filament feeding system by which Lycra was introduced to the wool fibre stream or with the SIRO system for spinning a yarn from two strands of roving. Lycra, which is fed under the delivery roller of the drafting system, enters the triangle 'V' formed by two drafted strands of roving which wrap around the Lycra filament. Before being fed to the triangle 'V' Lycra is stretched to 3-4 times its initial length because of difference in rotational speed between the unwinding pair of rollers and the delivery pair of rollers. The core yarn packages are then subjected to a stabilising treatment to set the twist of the yarn and position of the wrapping fibres around the core. In the spinning experiments, Lycra of linear densities 22 dtex, 33 dtex, and 44 dtex was used for the core, whereas the wrapping was provided by 100% wool roving 220x2 tex and 250x2 tex and a 200x2 tex roving composed of 45% wool and 55% PES.

VARIANTS OF EXPERIMENTAL CORE YARN AND TEST RESULTS

The effect was tested on the properties of the obtained core yarns, of the following technological parameters: linear density of Lycra; tension of Lycra while being merged

with the staple fibre stream; and twist of the yarn as expressed by α_m . The experimental variants of core yarn with Lycra included yarns with 100% wool wrapping, of linear densities 13.9x2 tex and 15.6x2 tex, and yarns with a wrapping 45% wool and 55% PES, of linear densities 10x2 tex and 12.5x2 tex. A SIRO-type yarn with a Lycra core shows the following differences compared to a conventionally spun wool/Lycra core yarn incorporating a yarn with Lycra and one without Lycra plied together: arrangement of the staple fibres in the wrapping; position of the Lycra core following the tension-relaxation cycle; and location of the core in the cross-section of the yarn. Upon removal of tension, the Lycra core of the conventionally spun yarn has no wrapping in contrast to the SIRO-spun yarn where wrapping is retained. In the cross-section of a conventionally spun yarn the Lycra core lies outside the staple fibres, while in a SIRO-spun yarn it is surrounded by the staple fibres.

The presented results show that the tensile properties of the yarn are largely dependent on the parameters of the core. The highest tensile values were recorded for the yarns in which the Lycra core was 44 dtex. A finer Lycra core, 33 or 22 dtex, can be used if the buyer is expressly in favour of a lower proportion of Lycra in the yarn.

The effect of the degree to which the Lycra filament, 44 dtex and 33 dtex, is stretched before being combined with the staple fibre on the real proportion of Lycra in the yarn was determined, using as an example the yarn of a linear density of 15.6x2 tex with 100% wool wrapping. The test results were then compared with the calculated values of Lycra content. The highest proximity of the results was recorded if the 33 dtex Lycra was stretched to 3.3 times and the 44 dtex Lycra was stretched to 3.7 times its original length.

The effect of twist of the yarn on its tensile properties was analysed for the wool yarns 13.9x2 tex and 15.6x2 tex and the results are presented in Table 1. The results suggest that the optimum twist levels for wool yarns spun with a Lycra core are $\alpha_m = 130 \div 134$. The level of elasticity was tested for the 13.9x2 tex yarn with 100% wool wrapping and 12.5 tex yarn with 45% wool and 55% PES in the wrapping. The yarns were made in three variants of linear density of the Lycra core, 22 dtex, 33 dtex, and 44 dtex. At a maximum load of 200 cN all variants showed a high elasticity value ranging from 71% to 84%. The lowest value of elasticity was recorded for the yarn in which the Lycra core had a linear density of 33 dtex.

SUMMING UP

1. The proportion of Lycra in the yarn is dependent on the linear density of the yarn, stretch of the Lycra filament before its being merged with the staple fibre stream, and – to a lesser degree – on the twist of the yarn;
2. The tensile properties of the core yarn are dependent on the linear density of the Lycra core and twist of the yarn. The highest values of tensile strength were recorded for yarns with a Lycra core of 44 dtex, twisted to $\alpha_m = 130 \div 134$.
3. Lycra core of a linear density of 22 dtex, 33 dtex, or 44 dtex in wool/Lycra core yarns ensures a high degree of elasticity of the yarns, and the clothes made from such yarns are characterised by permanency of shape and wearing comfort.

Table 1 – Effect of twist on parameters of yarn of linear density 13.9 x 2 tex and 15.6 x2 tex

Parameter	Yarn 13.9 x 2 tex with 22 dtex Lycra			Yarn 15.6 x 2 tex with 44 dtex Lycra			
Metric twist factor α_m	119	123	134	114	118	126	130
Real twist (T.P.M.)	704	737	820	678	686	716	752
Real proportion of Lycra (%)	3.7	3.1	3.3	5.3	4.8	4.7	4.5
Breaking tenacity (cN/tex)	6.7	6.8	7.2	7.5	7.6	7.5	7.8
Elongation at break (%)	9.4	8.8	8.2	13.5	13.3	15.7	18.2

P1.6.

X-RAY DIFFRACTION , I.R STUDIES AND SOME PHYSICAL PROPERTIES OF ANNEALED SILK FIBRES

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The degree of crystallinity and internal microstrain of annealed silk fibres have been measured by X-ray diffraction technique. The degree of crystallinity is compared with that obtained from corresponding Infrared spectra, the degree of crystallinity tend to be increase with increasing the annealing time.

The behaviour of some optical parameters has been discussed in view of the crystalline state. The effect of annealing time at a constant temperature on the optical and structural nature of silk fibres has been clarified.

P1.7.

LIFE CYCLE ASSESSMENT OF COIR AND LATEX SEATS

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Botucatu - Brazil

Natural resources typically supply inputs to a product, process or activity life cycle in the form of energy and raw materials. It could be mentioned the impacts to ecosystems and human health associated with the use of natural resources, e. g., the loss of assimilative capacity, habitat destruction, aesthetics and climate change.

The term *resources* refers to any component of the natural environment, including air, water, land and biomass, used as an input to the system under evaluation (SETAC, 1993)¹.

The concept of depletion refers to the idea that the reserves ^a, stock ^b, or flow ^c, of a resource are being diminished or impaired by human activity in such a way that the resource can no longer serve as input to the system under consideration. The direct impacts of the depletion of a resource are the reduction in opportunity for future generations to access it; the burden it may place on substitutes; and the inability to pursue the activities upon which it depends.

According to Reis, M. J. L. (1996)², environmental legislation, even if considering the differences among countries, states or regions of a same country, has been imposing more and more severe conditions with heavy penalties and rigid conditions for licensing of installation and operation of production units. On the other hand it has also been used to reduce the competitive disadvantage of those who have been looking for a responsible way of working. Consumers, mainly those from the first world countries, are rejecting products which are considered environmentally harmful determining favorable position to the use of less aggressive productive processes. Such processes may have additional costs but it does not affect competitiveness which creates healthy products and services what makes consumers pay a bit more for products with approved Environmental Quality.

As a result the so called "green stamps" came into being which sometimes grant to a product a kind of "diploma of good behavior" but do not guarantee that the permitted criterions are being strictly followed to support the certification. There are several cases of products which in order to get a piece in the market have been using ecological labels but with no justified guarantees (Reis, M. J. L., 1996)².

^a Standing quantity, mass, volume, or flow of nonrenewable and renewable resource.

^b Standing mass or volume of a nonrenewable reserve.

^c Resource for which natural qualities allow replenishment.

Today the companies are concerned about adapting themselves to an environmental aspect otherwise the risks of losing a space conquered with great efforts what makes it necessary to use environmental strategies according to supporting development.

According to NBR ISO 14001: 1996⁽³⁾ regarding Environmental management – Specification and Goals for usage, several organizations are concerned with having a correct environmental performance controlling the impact of their activities, products or services for the environment considering their policies and environmental aims. Such behavior is within a demanding legislation about economical policy development and other environmental protection positions as well as a growing concern from interested parts about environmental matters and supporting development.

Environmental matters are closely related to quality, total quality, intrinsic quality, pleasing consumers, employees and the environment. And these are also fundamental parts for a company survival. It is necessary to have the capacity to generate causes and effects related to production and also to ecosystem.

The first effective process of Life Cycle Assessment (LCA) were conducted in Europe and in the USA around the 70s when it was possible to observe the environmental effects of all life phases of a determined product evaluating since its raw material obtaining process until its final disposal. It was known as the evaluation "from cradle to grave".

The concept of life cycle assessment is very appropriate for an adequate evaluation of environmental impacts of a product being much wider than the known Environmental Impact Studies (EIS) whose limits are more restrict. According to Reis, M. J. L. (1996)² based on LCA it could be obtained the sum of quantified environmental effects being that the amounts are obtained through individualized analysis of selected phases for LCA:

- total gas exhausting
- total emission of effluents
- total energy consumption
- total residue generating
- total soil contamination

According to SETAC (1993)¹ an analysis of complete life cycle assessment considers the environmental impacts throughout a product's life since its extraction or raw material obtaining for production, usage and final disposal.

Table 1: Characteristics and Properties of coir:

Fiber length	15 to 33 cm
Fiber diameter	0,05 to 0,4 mm
Color	clear to dark-brown, reddish brown
Touch	hard, a bit rough
Prolongation (Lengthen)	very tall
Resistance	Dry: technical fiber 8 to 20 Km, thread 8 to 12 Km. Wet: 93% of dry resistance.
Density	very reduced for fiber has a great hollow space
Humidity absorption	Tolerance combined with humidity 13%
Lignification	Strong
Tingible	very good although, using colors which allow good coating.

Font: Harries, N. G. & Harries, T. E. (1976)⁴

The coconut tree is considered worldwide as the "life tree" due to its several usage and ends. It is a rich source of food and energy and is used for housing, furniture, and cosmetic, margarine, fiber and soap industries as well as handcraft. It guarantees a foreign market business for producer countries through exportation of its mainly products: pulp and oil besides assuring several employment position direct and indirectly. In Brazil the demand for several kinds of vegetable oil comes from the annual crops of soyabean and corn and coconut is lead mainly for food in both forms "in nature", as the water of the green fruit or domestically using the dry fruit, and the industrialized products (Ferreira, J. M. S. *et al*, 1994)⁵.

The coconut tree, according to Ferreira, J. M. S. *et al* (1994)⁵, is thoroughly used: root, stipe inflorescence, leaves, palmae and mainly the fruit which by simple transformation generates several byproducts which may be classified in three groups:

- products used for food using the fruit pulp;
- fiber products used mainly by the textile industry; and
- several other products of smaller importance.

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P1.8.

RADIATION STIMULATION REACTIVITY DIFFERENT TYPE OF CHEMICAL PAPER-PULP APPROPRIATELY FOR PRODUCTION OF DERIVATIVE.

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Electron beam treatment has become accepted as industrial techniques wide range of operations such as product sterilization, polymer-composite curing, flue gas treatment, destruction of hazardous wastes.

In the last years the increasing interest is observed in radiochemistry of cellulose. The radiation treatment has been used for modifying wood, paper and textiles by radiation grafting or creating. Another branch of application of electron processing is the modification of the pulp used in the viscose process, what significantly lower production costs and provide environmental benefits. Institute of Nuclear Chemistry and Technology, Pulp and Paper Research Institute and Institute of Chemical Fibres has taken on the common works which arise is elaboration of radiation methods for modification of paper pulp and production of useful cellulose derivatives such as cellulose carbamate, carboxymethyl cellulose (CM-cellulose), carbonate cellulose and methylcellulose.

In the scope of project the following investigations will be carried on:

- optimalization of radiation dose for electron-beam treatment of cellulose mass,
- determination of changes in molecular, supermolecular, morphological and chemical structure of irradiated cellulose samples,
- laboratory tests for verification of enhancement of cellulose reactivity in viscose production after e-b treatment.

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P1.9.

LIGNOLIT PROPERTIES AND APPLICATION

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In this paper the main assumptions are presented, concerning the production of new generation of wood-based products made from small size wood pieces, on the basis of solutions included in the patent concerning: The method of disintegrating plant stems, particularly of wood, in the process of producing ligno-celulose products and machines for this disintegration (Kokociński 1993).

The test proved that small size pine wood pieces disintegrated with the method of cyclic splitting can produce wood-based material of high strength quality.

The tested wood-based material due to its characteristic structure and high mechanical properties was given a transient name of lignolit (lignum-wood, lite-solid) – a wood-based materials with parameters resembling those of natural wood.

P1.10.

COMBUSTION CHARACTERISTIC OF WOOD PROTECTED BY INTUMESCENT COATINGS IN DEPENDING ON SWELLING ADDITIVES

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Intumescent coatings are the most efficient ways of fire retarding of flammable materials. The coatings swell under the influence of heat and form a thick porous charred layer. The coating perfectly insulates substrate against excessive increase of temperature and oxygen access. In order to make intumescent coatings effective, a proper selection of essential components, i.e. carbonizing, foam-producing and dehydrating materials, is necessary. The choice of components for an intumescent fire retardant composition has an essential effect on the rate of charred mass formation and its structure.

In the paper, the influence of different modifiers, added to amino resins during the process of condensation, on fire retardant and heat-insulating efficiency of intumescent coatings for wood, is presented. The research on efficiency of intumescent systems conducted at the Institute of Natural Fibres in Poznań allowed to determine the reactives responsible for membrane producing substance, caking agent, dehydrator and catalyst. Different molar proportions of reactive substances were used in different combinations of components. The conditions of condensation at variable pH, temperature and time were established.

The fireproofing efficiency was studied by determining heat release rate (HRR), effective heat of combustion (HOC), mass loss rate (MLR) and specific extinction area (SEA) during the combustion of samples investigated.

This paper also presents the thermal analysis of samples dynamically heated from 20°C to 900 C in the presence of oxygen. The results are presented in the form of DTA, TG and curves.

The most efficient coating, both from the point of view of fire retardancy and heat insulating properties, was found to be that based on amino resin prepared from urea, dicyandiamide and monoammonium phosphate and dextrin.

The exposition of wood coated with urea-dicyandiamide-phosphate-formaldehyde resin supplemented by dextrin to heat flux of 35 kW/m² for 30 minutes does not result in ignition and no increase occurs in heat release and mass loss rates and in effective heat of combustion.

P1.11.**MICROSTRUCTURE OF DENSE POLYMER MEMBRANES****H.Grigoriew¹, A.G.Chmielewski¹, H.Amenitsch²**¹ Institute of Nuclear Chemistry and Technology Dorodna 16
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Up today, polymer membrane designers does not take into account in permeation processes such parameters as structure of polymers and its changes influenced by penetrant. In last ten years our knowledge about such structures has developed very rapidly, what is mainly caused by introduction modern experimental methods of investigation. It was shown that very common effect existing in such materials is the microphase separation. The microstructure formed as self-organization of clusters and micelles influenced many macroscopic properties of these materials.

As an example of complicated microstructure in polymer-solvent system we present our last study. The creation of the microstructure was observed during our synchrotron studies of the system: dense cellulose membrane-water. We stated that the cellulose swelling results in creation of micelles. Temperature increase of the system leads to ordering the micelles in paracrystal-like array. Simultaneously, a lamellar-like ordering with decreased d- distance appears. The results are under elaboration.

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P1.12.

ENVIRONMENTALLY FRIENDLY RESIN BINDER SYSTEMS FOR SILICA SAND

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Chemically hardened processes for core-making industry have been widely used for many years and are successful because of high productivity and good quality.

Unfortunately these advantages are often gained at the expense of environmental risk, requiring difficult environmental engineering in the core room.

New resin binders, hardened with carbon dioxide or organic esters provide productivity and quality with environmental safety.

New binder systems are based on alkaline phenolic resins cured in ambient temperature.

In our work phenolic resins properties in relation to polycondensation terms and behaviour of binder compositions in relation to quality and quantity hardener systems will be discussed.

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P1.13.

IMMISCIBLE POLYMER BLENDS CONTAINING DIBUTYRYLCHITIN AS ENVIRONMENTALLY FRIENDLY MATERIALS

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Chitin is a biopolymer being second to cellulose produced by biosynthesis. It occurs in some animals, where it is an important constituent of the exoskeleton. The major factor limiting the original chitin utilisation is its insolubility in popular solvents.

Chitosan and dibutylchitin are products obtained by chemical modification of the chitin. Chitosan is soluble in weak acidic solvents and it forms a compatible one-phase blends with water soluble polymers. The chemical and morphological structures and physical properties of the blends of chitosane acetate salt with poly(ethylene oxide) and poly(vinyl alcohol) in solution and solid state were studied (1-5).

Dibutylchitin (diester of chitin) (4,6) is less known than chitosan but because of its excellent solubility in organic solvents has attracted some attention also as a biodegradable component of polymer blends for special use. In the present work the blends of dibutylchitin with polystyrene or polyacrylonitrile are prepared by casting from common solvent (dimethylformamide).

The immiscible blends of various compositions were obtained in special conditions. Their morphological and physical properties were obtained by TOA and DSC. Thermal degradation of the blends is presented using the thermogravimetric analysis.

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P1.14.

SYNTHESIS AND PROPERTIES OF HYDROPHOBICALLY ASSOCIATING POLYAMPHOLYTES

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Hydrophilic polymers, in which main chains are modified by a small amount of hydrophobic fragments, can associate in aqueous solution. Such polymers are used in many applications including microencapsulation, catalysis, paint formulation, and enhanced oil recovery [1, 2]. In order to improve the thickening properties of these materials in high-salinity media, hydrophobically modified polyampholytes were synthesized by means of micellar polymerization [3]. The hydrophilic backbone of such polymers contains both anionic and cationic units. The influence of the composition of the reaction mixture (monomers proportion, surfactant charge, structure of hydrophobic monomer) on the properties of formed polymer was studied.

The aqueous solution properties of polymers were studied by turbidimetry, viscosimetry in the dilute and semi-dilute regimes as well as by fluorescence measurements. Above a certain polymer concentration one observes a strong increase in the viscosity with respect to that of the corresponding non-modified analog. The viscosity increase is also enhanced upon addition of low-molecular electrolyte. Shear-thickening behavior as well as rheopectic and thixotropic effects were observed. From viscosity and fluorescence measurements it was confirmed that associations in the solution take place far below the observed viscosity increase (intramolecular association), and they are promoted at high salt concentration. Above the critical aggregation concentration, intermolecular transient junctions can be formed and gel-like phase appears.

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P1.15.**AGEING AND OIL RESISTANCE OF PET FIBER-REINFORCED
CR/NBR BLENDS****S.H. Botros; A.F. Younan and M.M. Essa**Polymers Department, National Research Centre
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The importance of blending of two types of rubbers has been increased recently; because it has become a useful approach for preparation of materials with new desirable properties lacking in the component rubbers. On the other hand, reinforcement of rubber blends with fibers combines the rigidity of fiber with the elasticity of rubber. Nitrile rubbers (NBR), of high acrylonitrile content, are known for their excellent oil resistance. Whereas thermal resistance is a unique property of chloroprene rubbers (CR). Thus, to obtain rubber compound with satisfactory thermal and oil resistance, CR/NBR blend was prepared, and polyester fiber (PET) reinforcement of that blend was carried out, on a conventional open mill, in an attempt to enhance thermal stability and improving swelling behaviour of the blend. The effects of curing systems and CR/NBR blend ratios upon the physico-mechanical properties of the composites and upon their swelling resistance in motor oil and brake fluid were determined. The results reveal that a balance of properties was obtained upon blending. PET fiber reinforcement of the blend improves thermal stability and oil resistance of the composite, in motor oil and brake fluid. Also, CR/NBR (50/50) composite cured with CBS/S, showed promising results.

P1.16.

EFFECT OF FIBERS ON THERMAL STABILITY AND SWELLING BEHAVIOUR OF CR/NBR COMPOSITES

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Reinforcement of rubber with fibers has become very important because of its processing advantages and its technical properties. The composites are of great interest in many industrial applications, notably the production of hose, oil seal and complex shaped mechanical parts. Thus, it was interesting to study the effects of type, length and denier of fibers upon the thermal stability and swelling behaviour of CR/NBR composites. The effects of nylon-6 fiber loading up to 30 phr were tested in terms of mechanical properties of the composites and swelling in toluene and oils. Also, the reinforcement of white filled blends were examined. The results reveal that nylon-6 fibers improved mechanical properties, thermal stability and swelling resistance of 50/50 CR/NBR blends. Of all fiber types investigated, viscose fiber CR/NBR composite has the best swelling resistance in motor oil, while PET fiber- composite has the best swelling resistance in brake fluid. 15-30 phr nylon-6 fiber loadings showed promising results, and the white filled nylon-6 composites showed a significant reinforcement with regard to mechanical properties and thermal stability.

P1.17.

STUDIES OF THE SURFACE OF FLUORINATED CARBON IN THE ASPECT OF ITS CATALYTIC PROPERTIES

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Although fluorinated carbon (FC) was first synthesized in 1934, only recently it found an application to catalysis. It is also used as a cathode material for lithium cells, a lubricant and modifier of filled plastics. FC can be prepared from different carbon feedstocks such as active carbon obtained from various natural and synthetic starting materials, as well as from graphite, carbon black and fullerenes by subjecting them to the action of elemental fluorine. Fluorinated carbon is a highly hydrophobic substance characterized by high thermal stability and these properties make it an excellent material for support of catalysts for a number of reactions, e.g. hydrogen peroxide synthesis from hydrogen and oxygen [1], selective reduction of NO_x with hydrogen [2], airborne tritium cleanup [3], low-temperature deep oxidation of VOCs [4]. Studies carried out hitherto were focused on catalytic role played by platinum group metal and hydrophobicity of FC support in the reactions investigated. No attention was paid, however, to the properties of catalytically active centers on the surface of FC support, although their presence could affect catalyst selectivity. Our study was aimed at characterizing acid properties of hydroxyl groups, small number of which remained on FC surface after fluorination of carbon black support.

Three samples of fluorinated carbon (containing 10, 28 and 65 wt. % F) and one non-fluorinated carbon black sample were tested for their activity in such reactions of acid-base catalysis as alcohol dehydration as well as cracking and double-bond isomerization of hydrocarbons. No activity was detected for cracking of cumene, which requires the presence of strong Brønsted acid centers, and for isomerization of 1-butene, which can proceed on acid centers of moderate strength. This observation points to the absence of strong proton acidity on fluorinated surfaces investigated, contrary to the effect of fluorine on oxide surfaces, such as alumina, where OH groups become strong acid sites due to the effect of very electronegative fluorine. The FC samples were, however, catalytically active for 2-propanol dehydration which is the model reaction proceeding even on very weak acid centers. An attempt was made by applying a computational model at explaining why hydroxyl groups on fluorinated carbon surface are so weak Brønsted acid sites. Relatively simple molecules consisting of condensed aromatic rings, shown in figures below, were used in the model applied and the effect of fluorine atom presence on the energy of proton detachment was investigated. The calculations were performed by means of MOPAC 6.0 program package, using AM1 semiempirical Hamiltonian. Geometries of model molecules were optimized. Proton detachment energies were determined by adding heats of anion formation to those of single proton

and subtracting heat of formation of initial molecule from the above sum. The obtained values were compared with those known for a number typical Hammett indicators and by this means pK_a values of model molecules were determined (see Table 1).

Model molecules can have two kinds of OH groups: rim ones (phenol-type hydroxyls - Fig. A) and those formed as a result of the disappearance of double bonds (alcohol-type hydroxyls - Fig. B). In both cases, the presence of fluorine atoms at neighboring carbon atoms enhances acidity, but the enhancement is small and even in the case of phenol-type OH groups does not result in the formation of strong acid sites. This conclusion is in good agreement with results of catalytic activity measurements and shows that the simple model used in our study can serve for predicting some properties of fluorinated carbon in a satisfactory way.

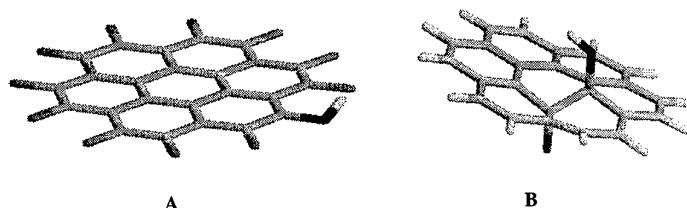


Table 1 - Results of calculations by AM1 method, obtained for models of carbon surface and Hammett indicators

Molecule	Proton detachment energy, kcal/mol	pK_a of Hammett indicators	pK_a calculated from linear regression
SH	276.20		16.22
EH	314.86		26.19
EH3	313.76		25.90
EH5	312.40		25.55
SF	247.91		8.93
EF	310.41		25.04
EF3	307.92		24.40
EF5	306.07		23.92
EF5M	271.27		14.95
TNA	257.63	12.20	11.44
DNA	273.64	15.00	15.56
NA	286.07	18.00	18.77
CIA	311.93	26.00	25.43

TNA - trinitroaniline, DNA - dinitroaniline, NA - nitroaniline, CIA - p-chloroaniline, SH - model molecule with OH group situated on the rim, SF - perfluorinated SH, EF - model molecule with OH group situated perpendicularly to the ring plane, EF3, EF5, EF5M similar model molecules with higher number of fluorine atoms, EH, EH3, EH5 - non-fluorinated analogs of EF, EF3, EF5.

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P1.18.

POTENTIAL APPLICATION OF BIOARTIFICIAL POLYMERIC MEMBRANES BASED ON POLYVINYL ALCOHOL AND SODIUM ALGinate FOR HEMODIALYSIS

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Blends of Biological and synthetic polymers constitute a class of materials called bioartificial polymeric materials. This combination gained great importance for biomedical applications as they pave the road to achieve new advantageous properties with respect to the single component.

In this research, blends of sodium alginate (SA) and polyvinyl alcohol (PVA) were prepared from their aqueous solutions. Membranes with different compositions were then prepared by solution casting. The produced films were cross-linked using bi-functional agent like glutaraldehyde (GTA) in acidic medium.

Hydrolytic stability of the films was evaluated by measuring the swelling ratio and the release of both the blend's components with time. Morphological analysis in conjunction with micro analysis revealed that the biological and synthetic components form a bi-phase system in which SA tends to separate in islands in the PVA rich phase. With high amounts of PVA, macroscopical phase separation can be observed. Thermally, blends were very stable till 180 °C as proved by the differential scanning calorimetry and thermogravimetric analysis. It is worthy to note that the dynamic elastic modulus of the blends increased exponentially as the increase of the SA content.

Selective transport properties of the blends using comparable hemodialysis solutes (sodium chloride, vitamin B12, and albumin) were examined. Films showed very promising results in comparison to that of the commercial membranes.

P1.19.

ENCAPSULATION OF LIVING CELLS TOWARDS ARTIFICIAL, HYBRID ORGANS

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Living cells protected from host immune system response in a manner of encapsulation inside polymer spheres can provide surrogate device for maintaining or replacement broken-down organs [1 - 5].

Many attempts to establish the preliminary conditions for the encapsulation of the living cells were done by our group. Cells immobilisation by gelation of the natural polymer - sodium alginate - was implemented. Spherical chamber structures of alginate, diameter between 2 and 3 mm, were formed. It was determined that the empty area inside the chambers is a favourable environment for the growth and proliferation of the yeast cells, contrary to the "solid" polymer matrix. The cells inside the spheres were protected against mechanical damage and unfavourable outside conditions by surrounding alginate layer. However, they were not protected against the immune system components. Thus, the studies concerning the preparation of the outer, synthetic coating has been carried out. This synthetic layer should protect the encapsulated cells against immune system of the recipient as well as should enable diffusion of nutrients and the other substances that stimulate natural action of cells. The additional coating was formed by means of immersing the capsules into acetone solution of poly(methyl methacrylate) and successive precipitation in water of this polymer on the surface of the capsules.

The preliminary *in vitro* biological tests have shown that used method could be a convenient tool for the encapsulation of the living cells. They are characterised by long-term survival and they are not damaged.

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P1.20.

SYNTHESIS, PHYSICAL AND CHEMICAL PROPERTIES OF URETHANE ELASTOMERS WITH CASTOR OIL PARTICIPATION

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The urethane elastomers are now preferred as polymeric biomaterials in connection with their excellent mechanical properties, the possibility of tailoring of hardness and elasticity avoiding use fillers or plasticizers and with relatively good hemo- and bio-compatibility, which arise from the chemical structure and hydrophilic – hydrophobic balance of the soft and hard segments of these polymers.

In our laboratory we obtain and investigate novel polyurethanes (PUR) based on oligoetherdiols (oligooxypropylene glycol, PPG or oligooytetramethylene glycol, PTMG), aromatic or cycloalifatic diisocyanates (MDI, SMDI), 1,4 – butanediol and triglyceride of ricinoleic acid (e.g. 12 – hydroxyoleic acid), the main component of the castor oil.

We expect, that use of the last substrat in PUR synthesis will lead to obtainig of the material with good hemocompatibility because of the greater affinity to albumins, counteracting the deposition of fibrinogen, which is the thrombus precursor. The PUR containing the incorporated lipid substance will be more close to the natural cell membrane, built from proteins and fats. The partial cross-linking of the obtained polymers and their intrinsic plasticization, connected with the structure of triglyceride of the fat acid, should have an advantageous effect on flexibility of the PUR.

The aim of our work was developing of the method of synthesis and investigation the PUR's obtained from different substrates, with or without catalysts, to determine if with regard to physical and chemical properties these polymers fulfill requirements of biomaterials.

The physical properties of obtained PUR's were checked by measuring of:

- the hardness and mechanical properties,
- glass and softening temperatures,
- thermal stability of the storage and loss moduli of the elasticity by use dynamic mechanical thermal analysis,
- contact angles with water and sorption of water.

The chemical stability of PUR's was investigated by measurements quantity and IR spectra of the extractibles arised after treatment the polymers by boiling water and boiling hexane, and by checking the pH change of water contacting PUR (24 h/70°C). The effect of hexane,

water, buffer solution and plant oil on the obtained PUR's were investigated by measurements of their tensile strength and by visual and microscopic observation. The thermochemical stability PUR's was checked by thermogravimetric analysis.

Table1. Physical properties of PUR's from 1,4-butanediol, castor oil and PPG, MDI(PUR-I) or PTMG, SMDI (PUR-II)

Properties	Units	PUR-I	PUR-II
Hardness	$^{\circ}\text{ShA}$	74	80 $\downarrow^{\text{d)}$
Stress at 100% elongation	MPa	9.0	8.3
Stress at 300% elongation	MPa	14.5	18.1
Tensile strength at break	MPa	27.4	56.2
Relative elongation at break	%	440	490
Glass temperature of the soft segments ^{a)}	$^{\circ}\text{C}$	-12	-57
Dynamic storage modulus of elasticity with bending, E'			
at 25°C			
at 40°C	MPa	14.7	97.7
at 100°C	MPa	11.3	52.5
Softening temperature ^{b)}	MPa	7.3	12.6
Contact angle with water ^{c)}	$^{\circ}\text{C}$	155	130
Sorption of water after 24h/ 38°C	$^{\circ}$	84 ± 2	-
	%	3.2	-

a) from maximum E'' (the loss dynamic modulus of elasticity);

b) from $\tan \delta = \frac{E''}{E'}$ deflection;

c) by sessile drop method with use of the goniometer;

d) diminishing response of instrument (flow under load)

P1.21.

A NEW COLLAGEN MATERIAL FOR THE REPLACEMENT OF CONNECTIVE TISSUE IN NEUROSURGERY

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Many different materials and tissues have been employed for dural repair. No ideal graft material is currently available. For many neurosurgeons cadaveric human lyophilized dura has been popular. Recently this material has been putatively associated with Creutzfeldt-Jakob disease.

A new Polish collagen composite implant for dura mater repair was obtained. The collagen dural substitute was made of hydrogel type I collagen reinforced with poly(ethylene terephthalate) mesh. Crosslinking of collagen and simultaneous sterilization of the final product were achieved by irradiation with an electron beam.

Collagen composite material has been used to replace, complete or strengthen the dura mater. Animals *in vivo* experiments and clinical studies have proven the excellent tissue compatibility of new Polish prostheses. Very satisfactory results were obtained after implantation of this substitute on patients with posttraumatic CSF-leakage and with intracranial neoplasms. The application of the prostheses in the surgical treatment of dysraphic defects on cerebral nervous system (CNS) in children makes it possible to approach large hernias, disqualified for operation so far. Neither allergy nor inflammations after operation in early as well as delayed-5,5 years observation was found.

A new Polish dural substitute seems to be better than other ones because of its similarity to natural dura mater. Besides, very good tolerance of collagen prostheses by organism and their parameters such as: mechanical resistance, watertightness, flexibility and conforming to anatomical contour, easy suturing and storing are important advantages in neurosurgical applications. Radiation-sterilized prostheses do not require any other treatment prior to their implantation, what is an important time-saving factor.

P1.22.

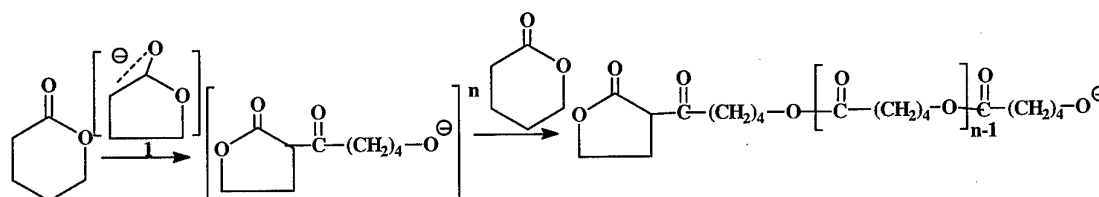
UNUSUAL POLYMERIZATION OF δ -VALEROLACTONE INITIATED BY γ -BUTYROLACTONE ENOLATE

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The polymerization of δ -valerolactone can be performed with anionic, cationic and coordination initiators. Living polymers have been synthesized with lithium *tert*-butoxide and other alkoxides used as initiators, as well as with potassium naphthalene complex with 18-crown-6 used as anionic initiators¹. In this communication unusual polymerization of δ -valerolactone initiated with γ -butyrolactone enolate initiator is reported.

γ -Butyrolactone is a dormant monomer and has been described as not being homopolymerized due to thermodynamic reasons, except in very extreme conditions (100° C and 20 000 atm.). However, the enolization of γ -butyrolactone via α -proton abstraction occurs easily². It turned out, that γ -butyrolactone enolates **1** initiate polymerization of δ -valerolactone (Scheme):



Similarly, Dale and Schwartz reported that enolization via α -proton abstraction should be also taken into account in the reaction of δ -valerolactone with a strong base³. Gitsov observed formation of enolates as intermediates in the polymerization of ϵ -caprolactone initiated by potassium naphthalene complex⁴. Thus the enolates can serve as initiators or intermediates in the polymerization of higher lactones yielding biodegradable polyesters as potential materials for medical and engineering applications.

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P1.23.

SYNTHESIS AND CHARACTERIZATION OF POLY[(R,S)-3-HYDROXYBUTANOIC ACID] TELECHELICS FOR BIOMEDICAL APPLICATIONS

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The term “telechelics” is derived from the Greek words *tele*=end and *chelos*=claw, and referred to oligomers possessing two identical reactive groups at both chain ends of a linear macromolecule. Such functionalized species may be prepared predominantly by anionic, cationic and group transfer polymerization (GTP).¹ The telechelict thus obtained can be used for further modifications by block copolymerization methods. Natural poly(3-hydroxybutanoic acid), [R]-PHB, and its natural copolymers are widely distributed in biological systems, being deposited in cytosolic inclusion bodies of many bacteria as an energy and carbon source. Many attempts have been undertaken in order to synthesize PHB and its copolymers via biofermentation or ring-opening polymerization of β -butyrolactone.²

The aim of the present work is to synthesize telechelic poly[(R,S)-3-hydroxybutanoic acid] containing respectively two hydroxy or carboxylic groups at both polymer chain ends.

Poly[(R,S)-3-hydroxybutanoic acid] telechelics containing hydroxy groups at both polymer chain ends were synthesized *via* ring opening polymerization of β -butyrolactones with γ -hydroxybutyric acid sodium salts/18-Crown-6 complex as initiator followed by termination of polymerization with bromoethanol or with bromodecanol, respectively. Poly[(R,S)-3-hydroxybutanoic acid] telechelics containing carboxyl groups at both polymer chain ends were synthesized *via* ring opening polymerization of β -butyrolactones with succinic acid disodium salts/18-Crown-6 complex as initiator followed by termination of polymerization by protonation. The telechelics obtained were characterized by ¹H and ¹³C NMR, gel permeation chromatography (GPC) and ESI-MS. The chemical structure of their end groups was additionally defined by tandem mass spectrometry experiments.

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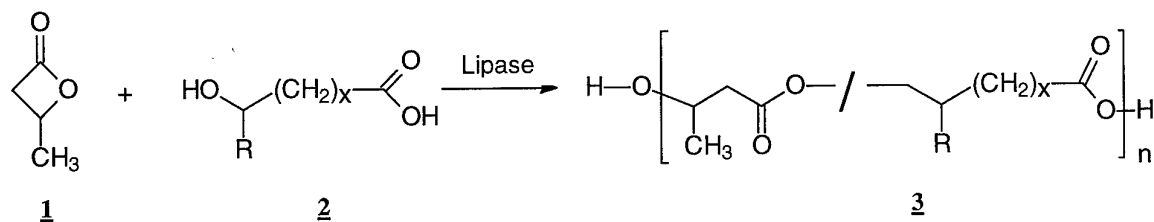
P1.24.

ENZYMATIC COPOLYMERIZATION OF β -BUTYROLACTONE WITH HYDROXY ACIDS – NOVEL SYNTHESIS OF POLY(3-HYDROXYBUTYRIC ACID) AND ITS COPOLYMERS

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The physiological activity of natural poly(3-hydroxybutanoic acid) (PHB) is believed to depend on its molecular mass, chain architecture and also on the chemical structure of the end groups [1]. Many attempts have been undertaken in order to synthesize PHB, and its copolymers via lipase-catalyzed ring-opening polymerization [2]. Different kinds of lipase have been used and a large variety of monomers such as hydroxy esters, hydroxy acids, diacids-diols, diols-diester were employed [3].

A novel route to polyesters, containing hydroxy and carboxylic end groups will be presented. Copolymerization of β -butyrolactone (**1**) with hydroxy acids: 3-hydroxybutyric acid (**2a**: R=CH₃, x=1) as well as 12-hydroxydodecanoic acid (**2b**: R=H, x=10) was carried out in bulk, using *Candida rugosa* lipase and porcine pancreatic lipase as catalyst:



Obtained polymers (**3**) with molecular weights from several hundred to several thousand, depending on both monomer used and the reaction condition were characterized by IR, NMR, ESI-MS and GPC.

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P2.1.

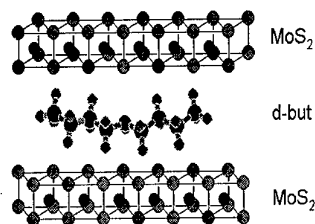
DIALKYLAMINES - MOLYBDENUM DISULFIDE INTERCALATES. SYNTHESIS, CHARACTERIZATION, AND ELECTRICAL PROPERTIES

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The synthesis and characterization of secondary amine-molybdenum disulfide intercalation products with electrical conductivities of about $10^{-2} \text{ S cm}^{-1}$ is described. A critical analysis of the geometrical criteria, usually used for determining the position of the guest in the interlaminar spaces, is furthermore attempted.



The reaction of secondary amines, diethyl-, dibutyl-, dipentyl-, N-isopropyl-, cyclohexyl-, and dicyclohexylamine, with a water suspension of MoS₂ exfoliated by a rapid hydrolysis of LiMoS₂ leads to the formation of layered organic-inorganic nanocomposites $\text{Li}_{0.1}\text{MoS}_2(\text{HNR}_2)_y$. Amine content (y) in the range 0.11-0.42 mol per mol molybdenum, as well as the interlaminar distances depend on the nature of the amine. Stoichiometry of the products, absence of water, and the presence of amine instead of alkylammonium ions are corroborated by thermal analysis and FTIR spectra of the products.

The electrical conductivity of compacted pellets between gold blocking electrodes were obtained by AC complex impedance measurements. Mixed conductivity nature of the products as well as their corresponding ionic conductivity component are determined by galvanostatic polarization of the sample between electron blocking electrodes.

These results, in addition to the comparison of the amine dimensions, calculated using building models considering both van der Waals radii of the atoms and an optimized molecular configuration, with both the experimental increase of the interlaminar spaces and obtained intercalation ratios lead to following conclusions: (i) During the intercalation process a contraction of the guest diameter is induced. (ii) Amine intercalation ratios for described organic-inorganic nanocomposites reach values near to the theoretically maximal ratios expected for the intercalation of a monolayer of the organic component. (iii) Electronic changes associated to the formation of the nanocomposites lead to products with high electronic conductivity.

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P2.2.

ELECTRON EMITTING NANOSTRUCTURES OF CARBON+PD SYSTEM

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Nanometer sized Pd crystals in matrix of various carbon forms were grown by thermal deposition of fullerenes C₆₀/C₇₀ mixture (C₆₀:C₇₀ ratio was 8:2) and Pd organic compound from two separated sources. Films were deposited on the various substrate (fused silica, copper band, molybdenum band and semiconducting Si). Obtained films were studied by TEM, ED, SEM and ESCA methods. The field emission in point-to-plane diode geometry was observed for film obtained on fused silica. The bias voltage caused the creation of electrical conduction paths. These paths were formed of the nanometer sized Pd crystals. As a result of such structural changes we observed enhanced field emission from the film.

INTRODUCTION

Field emission of electrons from various carbon films can occur at fields as low as few V/μm. For example for polycrystalline diamond film emission current of 10⁻¹⁰ A/cm² at the field of 6 V/μm was observed [1]. Some doped carbon materials can achieve emission at even 4 V/μm [2]. For example nitrogenation of carbon materials was investigated to show that nitrogen acts as n-type dopant [3,4]. In other technologies one search for inhomogeneous and rough film to enhanced field emission. We present the results of investigation of the influence of structural changes undergoing in consequence of the introducing electric field acting along the film, on the density of field emission current. We show that it is possible to obtain the emission current of 10⁻⁸ A/cm² at the field of 1 V/μm.

EXPERIMENTAL

Investigated films were obtained by thermal deposition from two sources containing C₆₀/C₇₀ mixture and Pd organic compound. C₆₀/C₇₀ mixture (8:2 weight ratio) and Pd compound were placed into separated Ta boats. They were heated (up to 573K) and evacuated to 10⁻⁵Torr for two hours before the deposition process. The substrates (Cu, Mo bands, n-Si and fused silica) were degreased before including it into the vacuum chamber. The deposition process was carried out under the pressure of 10⁻⁵Torr and at the temperature of 330-340K (the temperature measured on the surface of the substrate).

Obtained films contained ~60wt% of Pd. Pd contents were determined by energy dispersive spectrometry (EDS) and chemical analysis. All results for chemical compound analysis were calculated by full standards method with ZAF (mass number, absorption and fluorescence coefficients) corrections. Scanning electron microscopy (SEM) was performed with scanning microscope operating at 20 kV accelerating voltage and 3×10^{-9} A probe current. The electron transmission microscopy (TEM) studies were performed with transmission electron microscope operating at 200kV incident beam energy. The samples were moved from the layer directly onto 400 or 1000 mesh copper microscope grids. X-ray photoelectron spectra (XPS) were acquired in ESCALAB 210 spectrometer (at pressure of 10^{-10} Torr). Before these measurements the surface of the samples were cleaned with Ar^+ ion beam. The field emission measurements were performed with point-to-plane geometry in diode system. The "point" electrode was polished to obtained mirror-like surface with active surface $\sim 1 \text{ mm}^2$. Distance anode-cathode was 100 μm . During the measurements of electron emission current the vacuum of $\sim 10^{-5} - 10^{-6}$ Torr was maintained.

RESULTS

TEM images of the samples before field emission measurements show 2-4 nm objects homogeneously disperse in the observed volume. ED pattern of investigated area revealed diffuse rings which can be correlated with fcc Pd. XPS measurements exhibit Pd 3d5 peaks at 339.7, 337.7 and 336.0 eV as well as C 1s peak at 291.0, 290.3, 288.8, 287.3, 285.8 and 284.3 eV. The strongest C 1s peak (284.3 eV) could be attributed to carbon in C_{60} . Remaining, much weaker, peaks could be connected to oxidation effect of carbon. The binding energy of the

strongest Pd 3d_{5/2} peak (336.0 eV) is higher then for metallic Pd (335.1 eV [5]). The effect of lowering of binding energy as the result of the formation of Pd clusters was noticed by other authors [6-7] for Pd nanoparticles of size of 1.5-80 nm.

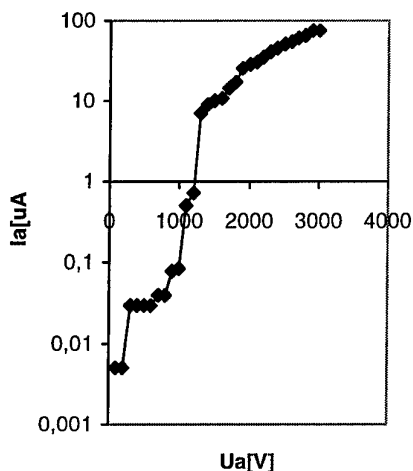


Fig.1 I-U characteristic of film after "break-down" (U_a-bias voltage anode-cathode, I_a – field emission current)

Field emission was measured in diode configuration and first it has not been observed. When the bias voltage had exceeded 2kV the field emission appeared and then, after such "break-down" it was observed as it is shown in fig.1. After the field emission experiment we observed, by SEM as well as TEM, formation of 10-20 nm Pd nanocrystals and creation of electrical conductivity paths composed of these Pd nanoparticles. Our conclusion is that the "break-down" is responsible for formation of Pd nanoparticles paths and existence of such paths enhanced field emission.

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P2.3.

NANOPARTICLES OF AMORPHOUS SEMICONDUCTOR IN TWIN INSULATOR MATRIX

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Since the classic works on amorphous semiconductors, it has been widely recognized that the electronic structure of covalent amorphous semiconductors (a-S) consists of localized states which form tails above and below the valence and conduction bands of extended states [1]. On the basis of the theory of localization of electron states, one can predict, however, that above a critical disorder all states in the bands may be localized [2]. The materials in which all states are localized are called amorphous insulators (a-I).

It was found that hydrogenated carbon-germanium (Ge-C) films prepared by plasma deposition from tetramethylgermanium (TMeGe) in the three-electrode reactor can exist in two different electronic structures [3]. A rapid transition from a-I to a-S is observed as a result of preparation conditions when they are monotonically changed. This effect results, for example, in a huge change in the specific electrical conductivity from 10^{-18} S/m to 10^{-3} S/m. A series of thin Ge-C films characterized by various electronic structure, from pure a-S to a-I, were investigated by means of modified Scanning Probe Microscope (SPM), X-ray photoelectron spectroscopy (XPS) and dielectric spectroscopy. The main purpose of this paper was to examine homogeneity of this materials in submicrometer scale.

The SPM is not only known as an excellent tool for imaging topography of materials with nanometer resolution but equipped with a conductive tip is fully exploited for charge distribution imaging and modification [4]. A gradient of electrostatic field induced by a non-homogenous charge distribution generates force attracting water molecules to the sample surface and as a result additional topography features occurred reflecting local charge density [4]. All samples were investigated as obtained - without prior charging. The SPM measurements indicate that our samples have a non-homogenous distribution of charge, most probably, due to different electrical properties of a-S and a-I areas. The globules of average diameter in the range 60 nm to 150 nm are observed. Their concentration in material depends on the preparation conditions. A step increase in the concentration is clearly seen when the change from a-I to a-S structure takes place. Most probably, the globules are grains of the semiconductor embedded in the insulator matrix.

The results of SPM correlate well with those obtained by means of XPS studies. It has been found that all lines related to both carbon and germanium atoms are split in the same way due to the differential surface charging. The ratio of the component lines depends on the type of film. The spectra obtained for a-I films consist mainly of the first component while the second one dominates in the a-S films. It is worth noting that the overall atomic composition for all samples is approximately constant.

Heterogeneous material consisted of components characterized by so different electrical properties is a grateful subject for ac spectroscopy. The complex permittivity measured for hydrogenated Ge-C films as a function of frequency fit well to the Bottcher-Trukhan model elaborated for the case of conducting particles in an insulating medium [5]. Both the semiconductor volume fraction and grains size, evaluated according to the model, confirm the previous results.

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P2.4.

RELAXATION PROCESSES IN ANISOTROPIC COMPOSITES OF LC-CELLULOSE DERIVATIVES

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Anisotropic polymer composites have been prepared by polymerisation of oriented lyotropic liquid crystal (LC) solutions in polymerisable solvent. The investigated composites consisted of cellulose derivative (CD) with poly(acrylic acid) or poly(methacrylic acid). Different cellulose derivatives (like propionyloxy-, hexanoyloxy-, and cyanoethyl-, hydroxy- propyl cellulose) capable of forming different interactions (dispersive, dipolar interactions or hydrogen bonds) with a second component were chosen. The anisotropy of the supramolecular structure was induced by shearing of thin layer of the LC solution of the CD in vinyl acid monomer. Then the anisotropy was fixed by photopolymerisation and its thermal stability was investigated by thermo-optical analysis.

The lyotropic solutions can be readily oriented by shearing. The most characteristic features of the oriented systems are their morphology and optical anisotropy which decays with time due to molecular relaxations. These systems have a characteristic banded texture with bands perpendicular to the shearing direction. The banded texture and optical anisotropy can be fixed in the composites by the photopolymerisation of acrylic monomer present in the lyotropic solutions. The anisotropic composites obtained on the basis of different cellulose derivatives show a significant difference in the thermal stability of their molecular orientation and optical anisotropy due to different intermolecular interactions between the components.

The molecular relaxations can be determined using several different techniques. In this study dielectric relaxation spectroscopy and dynamic mechanical analysis were used. These measurement techniques give complementary information about the molecular motion of polymers. The temperature dependences of the α -relaxations of the CDs follow the free volume theory (WLF) while for the β -relaxation of the polymerised vinyl acid the dependence is Arrhenius type. The molecular relaxations in the composites are very sensitive to intermolecular interaction, depending strongly on chemical structures of the CD.

Investigated materials show anisotropy not only of optical but also of mechanical properties. In the CEPC composites, the mechanical anisotropy is sensitive to the glass transition of CEPC, which results from the orientation of the CEPC chains. However, the

β -relaxation of the pAA component also affects the anisotropy due to some transverse bonds (interactions between polar groups). In the HPC composites one can observe mechanical anisotropy which increases at glass transitions of both components as well as at the β -relaxation of pAA. This effect is associated with transverse hydrogen bonds formed in oriented composites, which can be affected by molecular relaxations.

This work was supported by KBN project 7 T08E 066 14p03 (Poland).

P2.5.

THIN FILM SOL-GEL OF $\text{CeO}_2\text{-ZrO}_2$ THE CANDIDATE FOR COUNTER ELECTRODE IN ELECTROCHROMICAL DEVICES

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Thin films of mixed oxides of $\text{CeO}_2\text{-ZrO}_2$ with molar ratio $\text{Ce/Zr}=0.5$ have been prepared by sol-gel method. The precursor sols were prepared from a mixture of $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, $\text{Zr}(\text{OPr}^i)_4$ and isopropanol and then submitted to ultrasonic irradiation. The films were deposited by dip-coating technique on ITO-Asahi glass and densified at 80°C during 15 min and 450°C during 15 min in atmosphere of oxygen. Their possible use as ion storage (counter electrode) in electrochromic devices was studied by electrochemical measurements like cyclic voltammetry and chronoamperometry. The reversibility of the insertion/extraction process and the stability of the films as a function of the cycles number was performed. Also were realized thermal analysis (DSC/TGA), infrared spectroscopy (IR) and X-ray diffraction in order to characterize the gel.

INTRODUCTION

Thin films of mixed oxides of $\text{CeO}_2\text{-ZrO}_2$ are very interest candidates as counter electrodes to be used in electrochromic smart windows, due to their electro-optical performance [1]. These films remain colorless in the insertion/extraction process contrary to Nb_2O_5 [2] or WO_3 [3] thin films which change their optical transmission from transparent to deep blue in similar electrochemical conditions. In this work we report on the preparation and characterization of $\text{CeO}_2\text{-ZrO}_2$ films dip coated on ITO Asahi-Glass from a sol easy to prepare. Xerogels of $\text{CeO}_2\text{-ZrO}_2$ have been characterized by differential thermal analysis (DTA/TG) and X-ray diffraction and the coatings by scanning electron microscopy (SEM), atomic force microscopy (AFM), optical and electrochemical techniques.

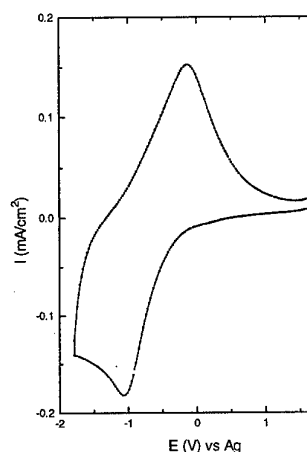
EXPERIMENTAL

The starting solution to produce $\text{CeO}_2\text{-ZrO}_2$ thin films with molar ratio $\text{Ce/Zr}=0.5$ was prepared by dissolving ammonium hexanitratocerate ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$) powder and zirconium isopropoxide ($\text{Zr}(\text{OPr}^i)_4$) in isopropanol in a small Becker recipient. The solution mixture was submitted for a few minutes (~5min) to the action of 95 W ultrasonic irradiation from a Sonicator[®] W385 Heat System-Ultrasonic, Inc. at 20 kHz equipped with

a 1/2" Disruptor Horn resulting in a transparent solution. The coatings were deposited by dipping on ITO coated glass substrates (Asahi-Glass, $14\Omega/\square$) previously cleaned and rinsed with bidistilled water, ethanol and then dried at room temperature, into the solution in ambient atmosphere ($RH < 60\%$) and withdrawing it at a rate of 12cm/min. The samples were subsequently dried in air at room temperature for 15 minutes. The uniform gel films were then densified at 80°C for 15 min. and kept the final temperature in oxygen atmosphere at 450°C for 15 min. The resulting coatings with a thickness of about 100nm for 1 dip were transparent and homogeneous without any visual cracking.

RESULTS AND DISCUSSION

The typical cyclic voltammograms (Figure) were registered for the 50th cycle between -1.8 and +2V vs Ag at a scan rate of 50 mV/s. This figure shows the cathodic wave maximum at -1.0V that correspond to the insertion of Li^+ ions and the anodic wave due to the Li^+ extraction at -0.1V. The insertion/extraction process does not change the color of the film which remains transparent. The anodic and cathodic charge density were measured from the integration of the cyclic voltammograms as a function of the number of voltammetric cycles. The exchanged charge which was equal to 4.2 mC/cm^2 for one layer film is very stable and does not change during the 500 voltammetric cycles.



CONCLUSION

The sonocatalytic method was used for the preparation of stable, cheap and easy to prepare cerium-zirconium sol based on $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ and $\text{Zr}(\text{OPr}^i)$ precursors. Sol-gel CeO_2 - ZrO_2 films obtained from this sol exhibit good electrochemical properties with charge density of 4.2 mC/cm^2 . The films present a reversible insertion/extraction kinetics of Li^+ ions without color change of the film. This property confirms their use in electrochromic devices as storage -counter electrode.

ACKNOWLEDGEMENTS: CNPq and FAPESP.

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P2.6.

A NEW APPROACH TO THE SYNTHESIS OF POLYMERIC NANOGELS

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Submicron-size polymer particles and gels (nanogels), having numerous applications in medicine and pharmacy (e.g. [1]), are usually obtained by polymerization. A drawback of this method is the necessity of applying further procedures to remove potentially harmful substances as unreacted monomer, initiators, stabilizers, etc.

A new one-step procedure involving radiation technique has been developed to synthesize polymeric nanogels. Dilute, deoxygenated aqueous solution of a hydrophilic polymer is circulated through an irradiation cell, where high-dose pulses of fast electrons are applied with a given frequency. After each pulse many radicals are formed on each polymer chain in the irradiated volume. Their intramolecular recombination leads to the formation of internally crosslinked macromolecules, i.e. nanogels. The transition from a flexible, linear chain into an internally crosslinked structure has been followed by laser light scattering and viscometry. When proper conditions are set, the molecular weight of the polymer remains almost constant, while the radius of gyration of macromolecules and the solution viscosity decrease, indicating the formation of more compact, crosslinked structures.

The new method has been tested so far on poly(vinyl alcohol) [2] and poly(vinyl pyrrolidone) [3]. Current work is focused on the synthesis of stimuli-sensitive nanogels, able to respond to changes in pH, ionic strength and temperature.

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P2.7.

MÖSSBAUER AND FT-IR SPECTROSCOPIC STUDIES OF MARIA SPAINSH COAL PYROLYSIS

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The absence of coal as fuel in industry refers to the fact that the atomic hydrogen to carbon ratio (H/C) of coals is relatively low (0.6 to 1.0) in comparison with those reported for liquid (4.0) and/or gaseous fuels (3.5-4.0).

Further, Coal conversion technologies such as gassification and liquefaction creates many environmental pollution problems arising from the presence of iron sulfur minerals, mainly from pyrite FeS₂.

The aim of the present work is to study the thermal degradation behavior of Maria coal from Teruel, Spain, through pyrolysis with special attempts addressed to (1) minimize the iron sulfur in the char. (2) Increase its calorific value by using respectively the methods of Mossbauer and FTIR spectroscopy.

Pyrolysis runs was carried out in a fixed bed reactor in Argon atmosphere. Selected sample (10-20 g) was heated up to 600 °C with a heating rate of 10 °C /min. Thermogravimetric analysis (TGA) is also given. High calorific value, total sulfur, pyretic sulfur and sulfates have been determined based on standard methods.

The Mossbauer measurements were performed at room temperature using conventional type mode spectrometer with ⁵⁷Co (Rh) radioactive source. FTIR spectra were recorded by co adding 64 scans at a resolution of 2 cm⁻¹ in a Nicolet magna 550.

The Mossbauer spectrum of the raw coal sample showed the presence of Fe²⁺ in pyrite and Fe³⁺ in jarosite, which had resulted from weathering effect. The Mossbauer spectrum of the produced char showed the transformation of pyrite to pyrohotite Fe_{1-x} S, while no substantial changes was observed in jarosite. S/Fe atomic ratio of pyrohotite have been calculated from its Mossbauer spectrum.

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FTIR spectrum of Maria coal gives a typically IR spectrum corresponding to a sub-bituminous coal with a high mineral content, mainly kaolinite, which is altered during pyrolysis due to the loss of hydroxyl groups. The pyrolysis of Maria coal produces also a marked reduction of the intensity of the aromatic band.

P2.8.

METHOD FOR ORIENTATION OF POLYPROPYLENE MATRIX IN BLENDS WITH LIQUID CRYSTALLINE POLYMER

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INTRODUCTION

Recently a great interest is paid to blends of liquid crystalline polymers and engineering polymers (EP) because such blends can be processed and reprocessed by standard methods as extrusion and injection moulding leading to products with new properties. The presence of LCP enhances significantly physico-mechanical properties for lower costs. Their properties are dependent on both orientations^{1,2} of LCP and a matrix. The orientation of LCP can be relatively easily reached by mechanical processing or by action of the magnetic (MF) or electric field (EF) during solidification^{3,4,5,6,7,8}. The changes in LCP orientation should implicate the changes in orientation of iPP matrix.

The aim of this work was to investigate the behaviour of the polypropylene/liquid crystalline polymer blends in the DC electric field and determine an influence of EF on orientation of polypropylene matrix.

EXPERIMENTAL

We used blends (iPP/LCP) of isotactic polypropylene (iPP) and liquid crystalline polymer (LCP), which was copolymer of poly(ethylene terephthalate) and poly(p-hydroxy benzoic acid) (PET/PHB). Two types of mixtures were prepared with 10% and 20% LCP contents. Samples for experiments were placed in thermally controlled apparatus and exposed to electric field. Orientation degree of iPP crystallites in investigated samples was measured on Rigaku-Denki diffractometer with textural attachment. The X-ray beam was perpendicular to the electric field direction (parallel to the sample surface). Orientational function coefficient (f_r)^{9,10} was calculated with method described by Wilchinsky¹¹ for isotactic polypropylene fibres. The orientation of iPP crystallites was analysed in relation to direction of electric field lines and was determined by fibre orientation parameter ($\cos^2\phi$) and orientation coefficient values for samples crystallised with and without electric field.

RESULTS AND DISCUSSION

In the sample containing the highest concentration of LCP and only thermally treated value of f_r changed up to 0 (random orientation).

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P2.9.

PROTON CONDUCTING POLYMER ELECTROLYTES BASED ON PHOSPHORYLATED PHENOLIC RESINS

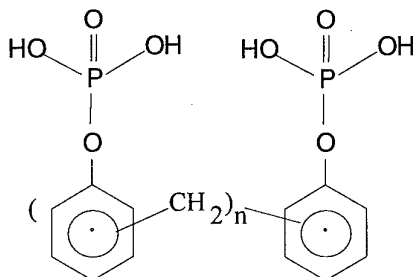
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There is demand for polymeric membranes of high protonic conductivity, which may be applied as electrolytes in fuel cells and various electrochemical devices. One of the methods for preparation of such solid protonic conductors is immobilization of proton donor (e.g. inorganic acid) in polymer matrix. For this purpose many systems based on complexes of phosphoric acid with linear and crosslinked polymers were investigated [1-3].

The aim of our work was to prepare proton conducting systems based on phosphorylated phenolic resins (PP resins):



PP resins due to their high acidity show good conducting properties. The presence of active hydrogens in phenolic units enables crosslinking of acidic component increasing chemical stability of the electrolyte. For example polyacrylamide hydrogels incorporating phosphorylated phenol-formaldehyde oligomers exhibit higher ambient temperature conductivities and better water resistance than analogous polyacrylamide / H₃PO₄ systems.

Some protonconducting systems based on PP resins will be presented and its properties from the point of view of application in fuel cells will be discussed

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P2.10.

CONTRIBUTION OF INTRA- AND INTERMOLECULAR INTERACTION TO NONLINEAR OPTICAL SUSCEPTIBILITIES OF POLYMERS

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Recently one can observe an increasing interest to polymers that possess high non-linear optical constants.^{1,2} To optimise the corresponding NLO susceptibilities it is necessary to perform complex experimental and theoretical quantum chemistry investigations both on the intra- as well intermolecular levels. Moreover, separation between vibrational and electronic contributions³ could play a fundamental role in understanding of contributions of corresponding bonds. The resignation of the existing approach⁴ is subsequent to make light of the strong intermolecular contributions of the long-range (solid state correlation interactions). As a consequence in the present work we propose to use advantageous of the both methods in order to clarify origin of the particular contributions. The methods consist in performance of strong *ab initio* calculations of electronic and vibrational hyperpolarizabilities within a separate molecule. To take into account intermolecular interactions we propose use step – by – step building of the super – molecule.

Afterwards we perform *ab initio* molecular dynamics geometry optimisation for the extend super-molecule and use effective molecular charges to carry out strongly *ab initio* band – energy calculations within the pseudopotential effectively introduced in the Ref. 4. As a consequence the long – range ordered contributions will be taken properly into account. Our calculations have shown that depending on the number of the polymer chains and kinds of the vibrational modes we have different values of the hyperpolarizabilities. Different solvents have been proposed to optimise the output hyperpolarizabilities. The role of the different donor and acceptors is clarified. Redistribution of the HOMO and LUMO states is closely connected with the vibration modes. The proposed method allows to propose the count in order enhance the output susceptibilities.

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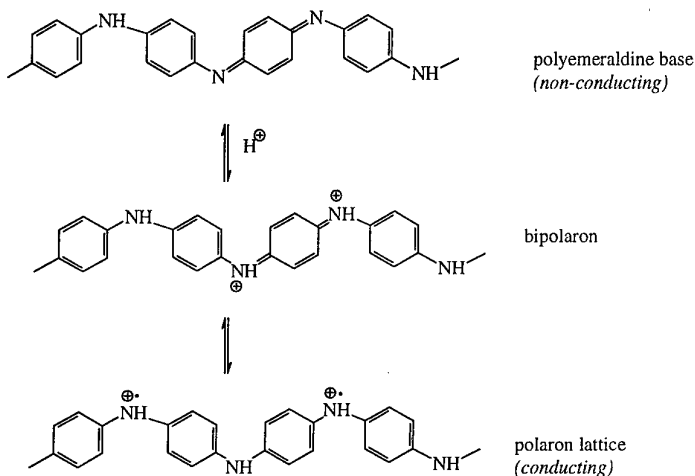
P2.11.

POLYMERIC BLENDS ABSORBING NEAR-INFRARED RADIATION

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Materials absorbing infrared radiation in the near-infrared region have been of great interest for many years. Such materials can serve in many applications, for example, as sensors, coatings, or in solar energy utilization. In most cases the absorbing material should also exhibit good film forming properties. Polyaniline (PANI) shows very high absorptivity in the near-infrared region. Polyaniline is a conjugated polymer, which becomes conducting upon protonation (Scheme 1), and the insulator-conductor transition is accompanied by significant changes in the UV-vis-NIR spectrum of the polymer [1]. Furthermore, it can be easily mixed and processed with other commonly used polymers as, for example, poly(methyl methacrylate), poly(vinyl chloride), polystyrene, cellulose derivatives, ABS or nylons [2].



Scheme 1. Protonation reaction of polyaniline (polyemeraldine base).

Protonation of polyaniline preferentially occurs in the imine positions with creating bipolaronic structure and is followed by immediate transformation of the created bipolaron to polaron [3]. The existence of the polaronic structure in the polymer is responsible for the absorption in the near infrared region. In this work, detailed studies of absorption in NIR region by polyaniline as well as its blends with poly(methyl methacrylate), polyvinyl

chloride, polystyrene, nylon and cellulose derivatives were performed. The great advantage of applying NIR spectroscopy is that it allows investigating all kinds of samples, from solutions of different concentrations to the optically transparent and opaque films. Additionally, subtle differences between NIR spectra can be observed. The addition of a protonating agent, e.g., camphorsulfonic acid to the transparent in the NIR region solution of polyaniline leads to a total drop of transmittance. The same effect of abrupt decrease of transmittance is observed when a film of the base form of polyaniline or poly-o-toluidine is soaked in any mineral acid (e.g. hydrochloric, phosphoric or sulfuric acid). Dependence of absorptivity of polyaniline on the protonation process brings on a great possibility to apply protonated polyaniline as an NIR-radiation-absorbing additive to the conventional polymers and polymeric coatings. Various blends with such commonly used polymers as poly(methyl methacrylate), poly(vinyl chloride), polystyrene, cellulose derivatives, ABS and nylons were prepared as a free-standing films by casting from chloroform or m-cresol. Figs. 1 show NIR spectra of PVC blends containing various amounts of polyaniline doped with diisooctyl phosphate (DiOHP). In case of all blends addition of more than 5 wt.% of protonated polyaniline in the blend causes total drop of transmittance of the film.

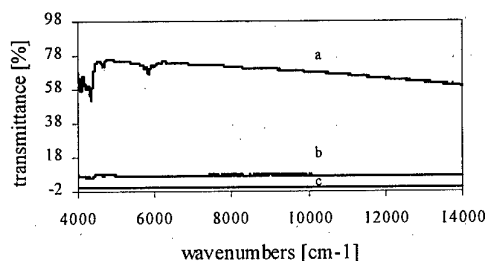


Fig. 1. NIR spectra of polyaniline blends with PVC: a) neat PVC film, b and c) PVC blends containing 2 and 5 wt% of polyaniline doped with diisooctyl phosphate (DiOHP), respectively.

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P2.12.**PREPARATION AND CHARACTERIZATION OF SOME
SUPERCONDUCTIVE CERAMICS / POLYMER 0-3 COMPOSITES****Nedilko S.A. and Bykov S.V.**

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The discovery of oxide ceramic superconductors in 1986 has led to creation of a wide variety of new materials with valuable properties. The superconductive ceramics / polymer composites represent one of the most recent attempts to combine unique magnetic and electric properties of superconductors with valuable mechanical properties of polymers. The preparation and characterization of superconductive ceramics / polymer composites have been reported by several research groups. In this report we present the results obtained in our work.

Oxide ceramics / polymer composites were prepared using $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ powder as a superconducting filler. As a polymer matrix were used such polymers as polyethyleneglycoldimethacrylate or its copolymer with styrene, poly(vinyl chloride), polystyrene and polycarbonate.

It was found that organic component do not generally affect magnetic properties (shielding and levitation) of the superconductive ceramics. At the same time such composites have increased stability and improved mechanical properties. These materials can be easily formed into desired shape in contrast to pure ceramics. It should also be mentioned that mechanical properties of superconductive ceramics / polymer composites may be changed in a wide range depending of polymer used as a matrix.

P2.13.

PHOTOCHEMICAL AND THERMAL CROSSLINKING OF POLYMERS

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Specimen of polyethylene (HDPE, LLDPE, LDPE and PVC) which have been modified with controlled formulations including stabiliser, initiator and crosslinking agent and subsequently blown as films and cast as plaques, have been subjected to natural weathering in an open desert climate in Riyadh, Saudi Arabia for periods of up to 75 days for comparison of results the artificial weathering was made. Subsequent analyses have been carried out using infrared and uv-visible spectroscopy and the effects of the additives on sample degradation with exposure time have been monitored. Whereas the uv-visible spectroscopic results indicate only broad changes in sample absorption with weathering exposure, the infrared measurements provide a specific molecular functionalities such as $>C=O$, $>C=CH_1$ $>CH_2$ with the presence of the additives.

The film specimens, some of which contain photo-initiator, stabiliser and crosslinking agent additives, have been monitored and the comparative effects of additive combinations with exposure times have been assessed. Unlike the polyethylene degradation in which the molecular specificity of the infrared spectroscopic technique was considered to be significant, the uv-visible technique provided better weathering data for the PVC system.

P2.14.

STUDY AND COMPARISON OF SECOND ORDER HYPERPOLARISABILITIES OF VARIOUS SERIES OF ORGANIC COMPOUNDS: TETRATHIAFULVALENE DERIVATIVES

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The application of nonlinear optical devices in telecommunication and photonics requires novel materials with optimized nonlinear susceptibilities. Materials with large nonlinearities are crucial for the development of all optical signal processing. Organic compounds with extended π -electron and electron donating and/or accepting groups are promising candidates for the mentioned applications^[1-3].

In this work, we study the second order hyperpolarisabilities γ of new N,N'-dimethylaniline tetrathiafulvalene derivatives using degenerate four wave mixing technique at 532 nm in picosecond regime. The obtained results are compared to those obtained previously for ethylenic, polyfluoroalkylsulfanyl-substituted, bis-dithiafulvenyl-substituted analogues of tetrathiafulvalenes. The molecular structures of the best compounds (in term of γ) in each series and their UV spectra will be presented. All these compounds display linear absorption at used intensity of light ($<1.8 \text{ Gw/cm}^2$). We use a theoretical model based on Maxwell's equations to deduce the third order susceptibility $\chi^{<3>}$ for each compound. A good agreement between the proposed theoretical model and the experimental results was found. All obtained γ for the studied compounds are larger than the γ of CS₂. The γ value for the best molecule (in term of γ) is about 10^5 larger than for CS₂ at the same wavelength. These compounds reveal large third-order nonlinear optical susceptibilities due to their highly conjugated framework and to the π -electron delocalisation and they are thus suitable materials for nonlinear optics.

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P2.15.

THE INFLUENCE OF THE TEMPERATURE ON THE OPTICAL SPECTRUM OF THE MODIFIED POLY(2-(9-CARBAZOLE)ETHYL METHACRYLATE) (PCEM)

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The synthesis of the polymer group containing carbazole as an element of the structure that generates the electroluminescence was performed. The physical properties of the polymers determined in the experiment suggest that the materials can be applied in the optoelectronic devices. The electroluminescence spectrum can be modified by changing substitutes in the carbazole either the donor or the acceptor group. Another way of changing the photoluminescence or electroluminescence spectrum is to shift the carbazole group aside by inserting the ethyl methacrylate group between the carbazole and the main chain.

Modified PCEM was the subject of the study performed to determinate PCEM's electroluminescence characteristics and the photoelectronic features and to analyze the possibility of using them in the LED structures. Investigations using those polymers have been carried out on the following subjects:

1. photoluminescent spectrum in temperatures from 80 K to 300 K
2. electroluminescent spectrum of the LED - type structures

Acknowledgements:

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P2.16.

MECHANICAL AND THERMAL PROPERTIES OF POLY(ETHYLENE 2,6 NAPHTHALATE) AND POLY(ETHYLENE TEREPHTHALATE) BLENDS

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The paper presents the results of investigations of mechanical and thermal properties of poly(ethylene naphthalate) and poly(ethylene terephthalate) blends. The measurement of tensile strength, elongation, impact strength and thermal properties has been presented in this paper. The analysis of the results is also shown. It has been observed that thermal properties of the blends improve with the increase in PEN share in the blends. The mechanical properties show the small increase with increasing the PEN share in the blends. Only elongation of the PEN/PET blends increase almost 300% comparing with PET.

INTRODUCTION

There has been a great interest in polyester blends from viewpoints of industrial applications and academic interest. Many studies¹⁻³ have been focused on the miscibility and transesterification in polymer blends. The same concern also the PEN/PET blends⁴⁻⁶ because in many industrial areas PET, PEN and their blends have been enjoying a wide variety of application for fibres, films and bottles. PET is an excellent material especially for beverage bottles and its blends with PEN are expected to be still better because, of their low permeability toward oxygen. Unfortunately PEN is also much more expensive than PET and this has limited its use. One potential approach for combining the attractive economics of PET with the better barrier and thermal properties of PEN is through blends of that polymers. In this paper the mechanical and thermal properties of PEN/PET blends and their phase behaviour was investigated.

EXPERIMENTAL

Samples used in this study were commercial grade PET with IV = 0,80 dl/g produced by Tongkook Corp. – South Korea and PEN with IV = 0,56 dl/g kindly supplied by Eastman Chemicals Company – Switzerland. The blends were prepared by injection molding using the Engel machine ES 80/20 HLS with L/D = 18 and D = 22 mm. The barrel temperature varied from 270-290 °C. The following blends have been prepared : (0/100, 5/95, 10/90, 20/80, 35/65, 50/50, 75/35 and 100/0 wt./wt.) PEN/PET. The tensile strength and elongation have been measured on INSTRON-1115 tensile machine, Charpy's impact

strength on impact hammer INSTRON - PW5, and Brinell hardness on the hardness equipment HPK 8206. The thermal analysis was performed on a Polymer Laboratories /England/ differential scanning calorimeter (DSC) and all scans were conducted at heating rate 10°C/min. The softening point of the blends has been measured using the VICAT methods. The applied load was 10N and the heating rate 10 °C/min.

RESULTS AND DISCUSSION

The results of mechanical properties of PEN/PET blends have shown the high increase of elongation with increasing the PEN share in the blends. The elongation has increased from 37% for PET samples to 180 % for PEN samples. It has been observed also the increase of impact strength from 5,2 kJ/m² for PET to 6,2 kJ/m² for PEN. The tensile strength has change from 54,5 MPa to 60,6 MPa. The hardness has decrease from 90 HB for PET to 80 HB for PEN. The all blends have shown very good elasticity together with good tensile strength and hardness. It should be mentioned that mechanical properties of PEN/PET blends strongly depend on processing conditions.

DSC study has shown double glass transition and melting temperature reflecting an inhomogeneous phase for all blends. The first T_g has been observed at 80 °C and it is responsible for PET glass transition, the second one at 121 °C and it is connected with PEN phase. Also the melting temperature has two peaks: at 252 °C- responsible for ET phase and at 266 °C- responsible for PEN phase. The double cold crystallization has been observed too. The DSC study allowed to determine the crystallinity of tested polymers and their blends. The crystallinity for PET was 27%, for PEN 38% and the blends have the crystallinity between 32-34%.

The VICAT heat resistance test shown the increase of softening temperature from 76°C for PET to 120°C for PEN. The blends have following temperatures: 10/90 PEN/PET – 84°C, 50/50 PEN/PET – 92 °C and 75/25 PEN/PET – 105 °C. This increase of softening temperature is very important because allowed to use PEN/PET blends for producing the bottles for hot filled beverages and juices .

CONCLUSIONS

Introducing the PEN material into PET allowed to obtain injection moulded pieces with high thermal resistance, very good elongation and impact strength and also good tensile strength and hardness. It is possible even for the blend with share ratio of the polymers between 30-70% were PEN and PET are immiscible. It must be remember that presence of PEN material in the blend cause the necessity of using the higher processing temperature and that the processing parameters have very big influence on the properties of producing injection moulding parts.

Taking into consideration the economic point of view, in industrial practice the blends with small PEN share in them can be only use.

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P2.17.

PIEZOCROMISM IN DOPED POLYPYRROLE**V. Skákalová¹, P. Fedorko¹, D. Végh¹, M. Hulman², O. Foltin³**¹CHTF, Slovak Univ. of Technology,
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We are reporting the data of the pressure dependence of the electrical conductivity of BF_4^- doped polypyrrole below atmospheric pressure. The pressure dependence has characteristics of a phase transition and is interpreted as a conformational coil-rod transition. The time response of the conductivity to a sudden increase of pressure, the existence of a glass transition as well as a sensitivity of the infrared and optical spectra of doped polypyrrole to variations of pressure (piezochromism) below the atmospheric pressure support this interpretation. The pressure effect should be considered in experiments with polypyrrole gas sensors.

P2.18.

**DESIGN OF PHOTOACTIVE MOLECULAR DEVICES
BASED ON QUANTUM CHEMICAL INVESTIGATIONS
OF PHENYLENEDIAMINE, CARBAZOLE,
TETRACIANOQUINODIMETHANE AND BENZENE MOLECULES**

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Quantum chemical *ab initio* design of photovoltaic elements and two variable logic functions of molecular digital computers are performing by using organic electron insulator, photo-induced electron donor and electron acceptor molecules and photoactive supermolecules.

The quantum chemical calculations and investigations of benzene (Ph), carbazole (Cz), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 1,4-phenylenediamine (PhDA) molecules were done using BPW91 and B3PW91 models of Density Functional Theory (DFT) in cc-pVTZ basis sets coded in Gaussian 94, Revision E. 2 with full geometry optimization. The calculations of molecular diads designed from mentioned above molecules and bridges: $-C_2H_2-$, $-N=N-$ were done using B3PW91/6-311G and Hartree-Fock/6-31G.

As an example we present here that according BPW91/cc-pVTZ calculation HOMO and LUMO of C_6H_6 molecule are respectively equal to -0.230 a. u. (-6.259 eV) and -0.040 a. u. (-1.089 eV) that confirm that the molecule is weak electron acceptor. HOMO and LUMO of PhDA molecule are equal to -0.164 a. u. (-4.463 eV) and 0.003 a. u. (0.082 eV) respectively that means that one is good electron donor. The analysis of results of calculations showed that usage DFT B3PW91 and BPW91 methods in cc-pVTZ is acceptable for molecule geometry calculations and can be used for the design of new theoretically aided supermolecules which in future should be synthesized.

The design of molecular photoactive diade PhDA- C_2H_2 -Ph is done based on the analysis of quantum characteristics of benzene and PhDA molecules. The results of optimization of interatomic distances and angles of molecular insulator bridge $-C_2H_2-$ showed that planes of PhDA and benzene molecule fragments are oriented by 1.177 and 1.923 degrees respectively the plane of the bridge fragment. Small negative charge equals to 0.031 e transfers from PhDA molecule fragment to the $-C_2H_2-$ and benzene molecule fragments. Therefore it can be expected that the electron charge should be transferred from PhDA fragment to benzene fragment during the diade excitation by light. The small charge transfer in ground state exists because of large value of condensed to bond all electrons between C atoms of bridge fragment. Calculations of the diade spectrum using configuration interactions single-excitation (CIS) Hartree-Fock method in 6-311G

basis set in first excited state showed that the diade should be excited by wave length equals to 282.31 nm. This enables to use this molecular diade for the solar energy converters.

Using our results of quantum chemical calculations were designed two supermolecules:

1) PhDA-N₂-TCNQ-C₂H₂-TCNQ-N₂-Cz and 2) Cz-N₂-TCNQ-C₂H₂-Ph-C₂H₂-Ph-C₂H₂-PhDA. Depending on the conditions of excitation and the outputting of transferred electron charge the 1) supermolecule might be Converse Unitary Negation-1, Converse Unitary Negation-0, Unitary Negation-1 or unitary Negation-0 two variable logic functions. The 2) supermolecule might be And, Nand, «0» as well as «1» Matrix Constants depending of the way of excitation and outputting the transferred electron charge.

P2.19.

QUANTUM CHEMICAL DESIGN OF MULTIVARIABLE ANISOTROPIC RANDOM-WALK STILBENE AND AZO-DYES BASED MOLECULAR DEVICES

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The quantum chemical simulations of two, three, four and six anisotropic random-walk stilbene and azo-dyes based molecular devices in ground state were performed by using *ab initio* Hartree-Fock (HF), Møller-Plesset (MP2) and Density Functional Theory (DFT) B3PW91 model methods in 6-311G** basis set.

Two variable anisotropic random-walk stilbene based molecular device is designed from carbazole (Cz), 1,4-phenylenediamine (PhDA), stilbene and TCNQ molecules joined with -C₂H₂- fragment bridges. The geometry optimization of bistilbene molecule was done by HF/6-311G**, stilbene molecule was optimized by DFT B3PW91/6-311G** and that was the basis for the design of stilbene based random walk molecular devices. The planes of phenyles are approximately 43 degrees twisted in ground state.

The two variable random-walk molecular device should be possible to excite by two different wavelengths that corresponds approximately wavelengths of Cz and PhDA investigated by CNDO/S-CI and ZINDO-CI computation methods. After excitation this supermolecule should be deformed by two different ways and after electron tunnelling to acceptor fragment TCNQ this molecule should dissipate the energy moving on the surface by two different ways.

Another kind of two variable random-walk device is designed based on one electron donor fragment and two electron acceptor fragments: Cz-C₆H₆-CH=CH-C₆H₆-TCNQ, NO₂. Three variable anisotropic random-walk stilbene based molecular devices are designed by such: Cz, PhDA, N,N,N',N'-tetramethyl-1,4-phenylene-diamine (TeMePhDA), stilbene and TCNQ molecules joined with -C₂H₂- fragment bridges or by another manner: Cz-C₆H₆-CH=CH-C₆H₆-TCNQ, TCNB, NO₂. Four variable anisotropic random-walk stilbene based molecular device is designed from Cz, PhDA, stilbene, TCNQ and TCNB molecules joined with -C₂H₂- fragment bridges. Six variable anisotropic random-walk stilbene based molecular device are designed as: Cz, PhDA, TeMePhDA, stilbene TCNQ and TCNB molecules joined with -C₂H₂- fragment bridges or: Cz, PhDA-C₆H₆-CH=CH-C₆H₆-TCNQ, TCNB, NO₂.

We have calculated DR1 azo dye molecule: $\text{NH}_2\text{-C}_6\text{H}_6\text{-N=N-C}_6\text{H}_6\text{-NO}_2$ (P. Lefin et al, Pure Appl. Opt., 1998, vol. 7, p.71). Geometry optimization was done using DFT B3PW91/6-311 model in ground state. The angles $\angle\text{CNN}$ of optimized molecule are approximately 114 and 115 degrees. In this molecule exist weak bondings between bridge nitrogen atoms and phenyle ring closest hydrogen atoms - something like intramolecule hydrogen bondings. These intramolecular hydrogen bondings keep molecule in almost one plane: only 0.015 and 0.005 degrees are between planes and -N=N- bridge. Exist also relatively large charge transfer from donor -NH_2 part to acceptor -NO_2 part: up to 0.12 electron charge in the ground state. That means that this derivative possesses the charge transfer band in excited state.

Based on DR1 azo dye calculation results were designed two variable random-walk molecular devices: Cz, PhDA- $\text{C}_6\text{H}_6\text{-N=N-C}_6\text{H}_6\text{-NO}_2$ and Cz- $\text{C}_6\text{H}_6\text{-N=N-C}_6\text{H}_6\text{-TCNQ}$, NO_2 , three variable random-walk devices: Cz, PhDA, TeMePhDA- $\text{C}_6\text{H}_6\text{-N=N-C}_6\text{H}_6\text{-NO}_2$ and Cz- $\text{C}_6\text{H}_6\text{-N=N-C}_6\text{H}_6\text{-TCNQ}$, TCNB, NO_2 , four variable random-walk device: Cz, PhDA- $\text{C}_6\text{H}_6\text{-N=N-C}_6\text{H}_6\text{-TCNQ}$, NO_2 and six variable random-walk devices: Cz, PhDA, TeMePhDA- $\text{C}_6\text{H}_6\text{-N=N-C}_6\text{H}_6\text{-TCNQ}$, NO_2 and Cz, PhDA- $\text{C}_6\text{H}_6\text{-N=N-C}_6\text{H}_6\text{-TCNQ}$, TCNB, NO_2 .

P2.20.

AZO CHROMOPHORE FUNCTIONALIZED POLYTHIOPHENES SYNTHESIS AND NONLINEAR OPTICAL PROPERTIES

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New polythiophene derivatives containing azo dye side group were prepared via copolymerization of 3-alkylthiophenes and Disperse Red 1 substituted thiophenes. Functionalized thiophene monomers were obtained from 3-thiopheneacetic acid or (7-thienyl-3-yl)heptanoic acid in the esterification reaction with Disperse Red 1. The presence of chromophore groups in the polymers was confirmed by ¹H, ¹³C NMR and FTIR spectroscopies as well as by elemental analysis. The introduction of azo dye as a side group to the conjugated polythiophene backbone significantly alters electrochemical and spectroelectrochemical behaviour of these compounds as compared to poly(alkylthiophene) homopolymers.

The obtained soluble polymer was processed into thin films by spin coating technique and its nonlinear optical properties were studied by the optical second and third harmonic generation techniques. The chromophore orientation was obtained by corona poling. Due to relatively low glass transition temperature a fast relaxation of induced order was observed. The third order nonlinear optical susceptibility was found to be slightly higher as that of non functionalized counterparts.

P2.21.

POLYMERIZATION OF OXIRANES BY POTASSIUM HYDRIDE AS A NEW METHOD FOR PREPARATION OF POLYETHERS

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The synthesis and properties of polyethers have occupied the attention of chemists for many decades. Polyethers play an important as commercial products and are a major subject of our research.

Recently it was found that polyethers can also be obtained via polymerization of oxiranes by potassium hydride [1,2]. In this method bifunctional polymers appeared to prevail over their monofunctional analogs. It means that the chain transfer reactions to monomer are limited or even did not occur in the polymerization of some oxirane monomers. The resulting structure is of great significance in using polyethers as components in polyurethanes synthesis. The absence of monofunctional chains improves the properties of final materials.

The polymerization was performed at 25°C under normal pressure, both in bulk and suspension in tetrahydrofuran. Complexing agents of metal cation *e.g.* crown ethers influence the reaction rate.

Depending on the of kind of monomers, the products are viscous liquid or solid polymers [3].

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P2.22.

NEW POLYETHERS WITH CARBAZOYL SUBSTITUENT AS A GOOD MATERIAL WITH PHOTOCONDUCTIVITY PROPERTIES

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It is known that carbazoles are the prototypical organic molecules that show an interesting physical and chemical properties. Carbazole plays its main role as a chromophore in polymeric system such as poly(N-vinylcarbazole) which is one of the sensitive photoconductive organic polymers [1, 2].

In this communication we report that novel polyethers containing a carbazole group explore its application in relation to the photoconductivity material.

New oligomers and polymers with various molecular weights were obtained via anionic polymerization and have been developed.

A fluorescence spectroscopy method was used to determine the range of emission with the Flurolog-3.12 spectrofluorimeter produced by Spex Jobin-Yvon (USA). Powder and diluted solutions in tetrahydrofuran of the monomers and their polymers have been examined. Excitation and emission spectra were recorded between 250 and 500 nm.

It was found that some monomers and their oligomers show intensive fluorescence in the range of blue light.

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P2.23.

LIQUID CRYSTALLINE EPOXY RESINS SYNTHESIS AND CURING

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Three series of liquid crystalline epoxy resins that contained biphenyl moieties as a mesogenic agent were synthesized:

- ① – by polyaddition of aliphatic diepoxides with 4,4'-dihydroxy-biphenyl. Diglycidyl ethers of ethylene glycol and 1,6-hexanediol were used,
- ② – by polyaddition of diglycidyl ether of 4,4'-dihydroxybiphenyl with aliphatic dicarboxylic compounds (ADC). Adipic acid, sebacic acid, a dimerized fatty acid and two polyesters with terminal carboxyl groups were applied as ADCs,
- ③ – by polyaddition of diglycidyl ether of 4,4'-dihydroxybiphenyl with difunctional aromatic compounds (DAC). Isomeric hydroxybenzoic and benzenedicarboxylic acids and diphenols were used as DACs.

The obtained epoxy oligomers were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy, and x-ray and FTIR spectroscopy. The effect of the composition and molecular weight of the resulting epoxy resins on liquid crystalline properties, phase transitions and morphology was investigated.

Ortho-tolylbiguanide was applied as the curing agent. The curing reactions were studied by differential scanning calorimetry, microscopic observations and FTIR spectroscopy. Depending on the temperature program of curing, it was possible to obtain polymeric networks with liquid crystalline order.

P2.24.

SURFACE COMPOUNDS: A SOURCE OF STANDARD GASEOUS MIXTURES OF VOLATILE ANALYTES

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Chemically modified inorganic materials found, among others, wide application as chromatographic supports, in solid phase extraction, gel electrophoresis and as materials for reinforced plastics. A new application of such materials for generation of analytical standards is the topic of the present study.

Silica gel or related materials were silanized and chemically modified to obtain surface compounds with thermally unstable organic residues. Thermal decomposition of these materials in a stream of a carrier gas resulted in a mixture with released volatile analyte. Concentration of the analyte varied depending on: the amount of modified silica gel, the carrier gas flow rate and on the temperature applied for decomposition. The so obtained standard gaseous mixtures were applied for calibration of analytical instruments like gas chromatographs, monitors or detectors. The advantage of the method consist in immediate generation of an analytical standard *prior* to the calibration step. This allows to overcome such drawbacks like concentration changes of the analyte during storage of the standard, side reaction of the analyte with accidental impurities of the medium, reactions with components of the vessels and adsorption. The surface modified supports are stable at ambient temperature and could be stored for years without decomposition.

The structures of the anchored residues were chosen so that the surface compound liberates only one volatile compound upon heating. The structures were also selected to maintain the desired, allowable decomposition temperature (below 350°). Surface compounds decomposing with release of carbon monoxide, carbon dioxide, ammonia and amines, thiols, isothiocyanates, ethylene, styrene, methyl chloride, methyl iodide and chloroform were obtained.

The advantages of the novel method of generation of analytes are: possibility of generation of wide range of compounds including toxic, irritant, malodorous or unstable analytes. Studies of the decomposition kinetics allows to study the reaction course.

P2.25.

EFFECT OF HEAT TREATMENT ON PHASE BEHAVIOUR AND MOLECULAR DYNAMICS OF MINERAL-FILLED PPS

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INTRODUCTION

Invaluable information about the morphology, nanoscale structure and chain order in polymers can be obtained from atomic force microscopy (AFM). This technique and other spectroscopic and microscopic methods are a good tool in the characterisation of polymers. In general, the molecular structure and morphology of the topmost surface layers (several nanometers thick) differ from those of the bulk polymer. Therefore, a comprehensive surface analysis is needed to correlate the surface structures with the physical/chemical properties of the composite material. The aim of this work is the observation of nanoscale structure and molecular dynamics of poly(p-phenylene sulfide) (PPS) and its composite.

EXPERIMENTAL

Atomic force microscopy and nuclear magnetic resonance spectroscopy (NMR) were used in the characterisation of the composite of PPS with silicon dioxide (SiO_2). Pristine PPS of Phillips Petroleum Company and SiO_2 synthesized¹ were mixed in the ratio of 20:100 and injection molded to the „cold” mold at temperature 50 °C. The same injection molding procedure was applied to the pristine PPS. The one part of both amorphous samples obtained were then heat treated at temperature 150 °C for 1 hour.

RESULTS AND DISCUSSION

Chosen results of the AFM experiment in constant force mode in the air of injection molded poly(p-phenylene sulfide) and its composition with SiO_2 are presented in figures 1 and 2. Extremely different results for pristine and composite polymer have been observed. Below glass transition of PPS ($T_g = 92$ °C) at the mold temperature 50 °C the crystallinity is very low², the AFM image shows very long agglomerates of average width about 1000 nm in scale 200x200 (nm^2) (Fig.1). Heat treatment at 150 °C for 1 hour increases the crystallinity² of PPS and simultaneously divides the big agglomerates on small aggregates which are being connected with very narrow bands. Between aggregates we observed in scale 250x250 (nm^2) a hole of depth 8 nm. The average diameter of aggregates is to about 150 nm and height approximately 8 nm. The width of the bands is about 20 nm. AFM data

PPS and silicon dioxide composite) (Fig.2 presented in the scale 2000x2000 (nm²) have much bigger agglomerates in comparison with pristine PPS. The average diameter of these agglomerates is 1500 nm. Annealing process at temperature 150 °C for 1 hour applied in this composite changes the surface morphology in the same manner as in pristine PPS. The size of composite aggregates is twofold bigger in comparison with polymer without the filler. Results of surface morphology of PPS and its composite are interpreted as an interfacial strain effects in the polymer network. There are probably a “weak” sections of morphological structure of polymer where the internal stress exists. This “section phenomenon” is in a good agreement with our NMR results.

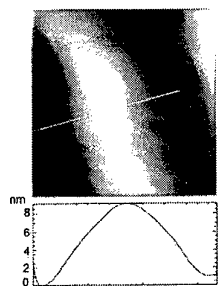


Fig.1. AMF in 2000×2000 (nm²) scale molded to the mold at 50 °C in scale 200x200 (nm²)

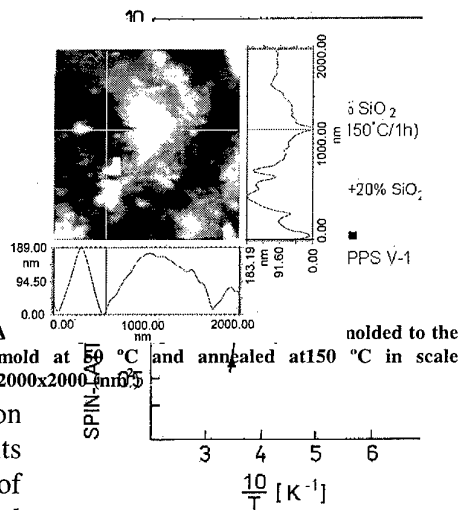


Fig. 2. A 2000×2000 (nm²) scale molded to the mold at 50 °C and annealed at 150 °C in scale 200x200 (nm²)

Pulse NMR measurements of spin-lattice relaxation time T_1 versus temperature for pristine PPS and its composite with SiO₂ have been performed. Results of measurements are shown in Fig.3. Exponential recovery of magnetization for pristine PPS suggests that the exchange of spin energy between aggregates is rapid in a results of a good contact between different phases of polymer. Introduction of filler to the polymer change the interaction mechanism. Non-exponential recovery of magnetization is observed. The contact between different composite polymer phases is weak. That means that the molecular reorientation of protons is independent in each of morphological phases.

CONCLUSION

AFM and NMR results of unfilled and mineral-filled PPS shows that fragmentation process during heat treatment in both materials have the same nature. Between agglomerates and smaller aggregates exist repulsion forces which are probably a source of fragmentation in the polymer network.

Fig. 3. Dependence of spin-lattice relaxation time T_1 versus reciprocal of temperature for pristine PPS, and filled PPS with SiO₂ and the last after annealing

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P2.26.

**THE INFLUENCE OF THE STRUCTURE OF HYBRID YARNA
GLASS/PA6 ON THE MECHANICAL PROPERTIES
OF COMPOSITES**

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The aim of research was to complete the comparative analysis between the structure and properties of yarns and mechanical properties of composites made from the yarns. The analysed yarns were made using texturing, commingling, twisting and friction spinning technology. The results of investigations indicate the main technological parameters of the production of yarns influencing strongly the tensile, bending and impact strength of composites glass/PA6.

P2.27.

THE USE OF CEMENT KLIN DUST AS A FILLER FOR SOME THERMOPLASTICS

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A large amount of cement klin dust is produced in cement factories. In this work a trial to get use of this dust was carried out. Samples of this dust were analysed and studied physically and chemically in order to be mixed with the polyethylene as a filler. It was mixed with recycled polyethylene in different ratio. Investigation of some mechanical and thermal properties of the thermoplastics has been determined after such blending. These properties are compared with other traditional filling materials and proved to be successful in substituting expensive used fillers.

P2.28.

STUDYING THE COMPATIBILITY OF CEMENT KLIN DUST IN THERMOSET BLENDING

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Cement klin dust is produced in the cement factories and filtered out of the exhaust gases in order to avoid the air pollution in the industrial. The collection and dumping processes are highly polluting to the environment. Practical uses of this fine cement dust had to be developed in order to get rid and to encourage cement factories transferring this waste to a by-product, that could be handled and sold in a pollution free manner. Due to the big percentage of fillers added to the unsaturated polyester blending process, this cement klin dust has been analysed and its compatibility with the matrix has been studied in order to investigate its effect on the properties of the thermoset blending process. General-purpose polyester was mixed with different proportions of the analysed cement klin dust. The physico-chemical properties of the investigated waste cement klin dust, as well as the strength properties of the polyester compounds containing this filler were determined.

P2.29.

CLAY AS A FILLER IN THE THERMOPLASTIC COMPOUNDING

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Conventional minerals are used as filling materials for thermoplastics compounding in order to ameliorate their properties and to deduct their prices. Calcium carbonate and talc are the major used fillers in polyolefine compounding in Egypt, while clay is completely neglected. This neglect is due to the shortage of information about the clay characteristics. The aim of this study is to investigate the physical and chemical composition of kaolinite extracted from Aswan in order to evaluate the possibility of using it as filler for thermoplastic compounding. This was added in different proportions to recycled polyethylene in order to investigate their compatabilities and their effect on the mechanical properties of the polymer matrix. The same has been compared with the conventionally compounded recycled polyethylene using calcium carbonate filler.

P2.30.

ATOMIC FORCE MICROSCOPY INVESTIGATION OF POLYSTYRENE AND POLYSTYRENE/PMMA COMPOSITES SURFACES

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The surface morphology of polystyrene (PS) before and after u.v.-irradiation was studied by means of Atomic Force Microscopy (AFM). The u.v.-irradiation of PS sample doped with poly(methyl methacrylate) caused distinct changes in surface morphology. The nanometer-scale structures of the rod-like shape bumps of diameter of 300 nm and the height of 75 nm were created.

I. INTRODUCTION

Physical and mechanical properties of plastics depend not only on the chemical structure of polymers but also on their morphology [1]. AFM technique is one of more suitable for characterisation of organic material surface [2]. Ultraviolet (u.v.) irradiation is one of the most destructive factors and it involves formation of radicals in macrochains followed by a breakdown of chemical bonds. The main reactions occurring in polymer upon its exposure to u.v. radiation are main chain scission, oxidation, side groups abstraction, etc. [3]. Because photodegradation of solid polymers starts in very thin surface layer, it is very important to use the technique enabling to monitor these surface changes.

In this letter, we present the results of our study of morphology changes caused by u.v.-irradiation of polystyrene (PS), polystyrene/poly(methyl methacrylate) blend (PS/PMMA). These materials are of interest because of its wide applications and looking for optimal preparation conditions. We were also interested in looking for the possibility of the nanometer-scale structures' formation.

II. EXPERIMENT

The PS was produced by Oświęcim, Poland. PMMA were obtained by emulsion polymerisation using ammonium persulfate as initiator. Thin polymer films were obtained by casting of 2% benzene solution onto glass plates. After the solvent evaporation samples were dried in vacuum to a constant weight. Then, the samples were u.v.-irradiated by a low-pressure mercury lamp TUV30W (Philips, Holland) during 8 hours. The intensity of

incident light (at sample surface) was 4.4 mW/cm^2 . All irradiations were performed at the room temperature in air atmosphere. The AFM experiment was performed on both non-irradiated and irradiated samples under ambient air condition using a combined AFM/STM system (OMICRON) working in the constant force topographic mode.

III. RESULTS AND DISCUSSION

AFM images of non-modified PS surface revealed an array of the randomly distributed holes of the typical diameter of $(100 \pm 25) \text{ nm}$, and the depth of $(1 \pm 0.2) \text{ nm}$. They were probably formed during fast solvent evaporation during film preparation. The individual bigger bumps of the diameter from few tens to few hundred nm appeared after irradiation. Their appearance can be explained by a diffusion of low-molecular gaseous blisters towards the polymer surface. When the tip was scanned a few times at the same area ($1 \mu\text{m}^2$) the parts of the top layer were removed and a small depression (1 nm deep) appeared as shown in Fig. 1. The mechanism of the material removal is most probably the result of abrasion via direct mechanical tip-sample contact. The study of nanometer scale modifications proved that using a force of 0.2 nN in AFM is enough high to modify the PS surface!

The most spectacular changes after u.v.-irradiation were observed in the case of PS/PMMA sample (Fig. 2). The domains in the form of big rounded bumps of $1.2 \mu\text{m}$ diameter and up to 80 nm in height were observed before irradiation. After irradiation the bumps become distinctly isolated and their shape was changed. The edges of these bumps become steep and their height become nearly the same for all of them and was about $(74 \pm 15) \text{ nm}$. The average diameter of these rod-like bumps was $(300 \pm 30) \text{ nm}$. The formation process looks like this one occurring during formation of self-organised semiconductor quantum dots.

IV CONCLUSION

We conclude that AFM can be effectively used for characterisation of surface nanostructures on irradiated polymers, as well as for their surface modifications in the nanometer scale. Moreover, phase shape and size as well as size distribution in case of immiscible polymer blends can be revealed directly by AFM.

Acknowledgements:

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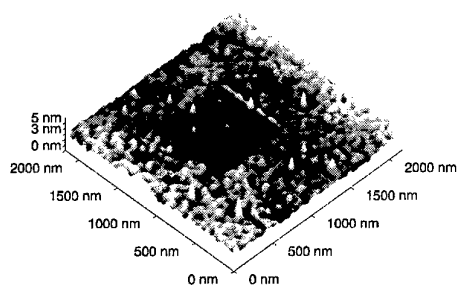


Fig.1. AFM quasi-3D image of $2\ \mu\text{m} \times 2\ \mu\text{m}$ area of PS after few scans of the same area of $1\ \mu\text{m}^2$ using a loading force of 0.2 nN.

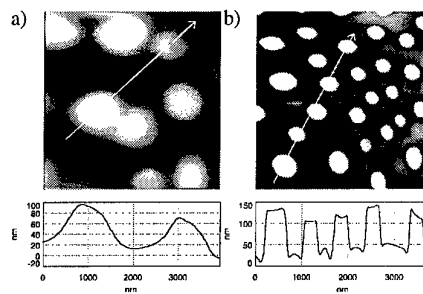


Fig.2. AFM top view images of $4\ \mu\text{m} \times 4\ \mu\text{m}$ area of PS/PMMA sample before (a) and after (b) u.v.-irradiation for 8 h.

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P2.31.

NEW ACRYLIC ESTERS, DERIVATIVES OF SOME DIGLYCIDYL ETHERS AS MAIN COMPONENTS OF LACQUER COMPOSITIONS

Wawrzyniec Podkościelny, Andrzej Bartnicki

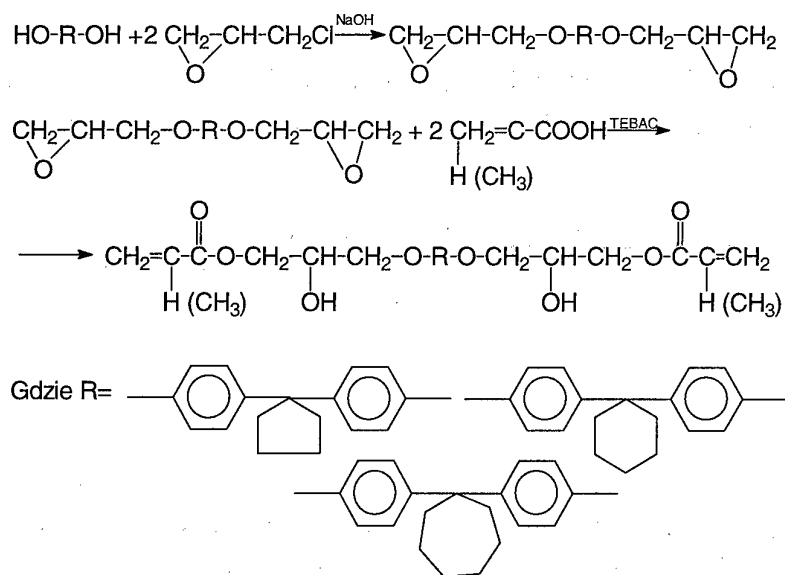
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UV-CURABLE COMPOSITIONS CONSIST OF THE NEW ACRYLATES OF DIGLYCIDYL ETHERS WITH REACTIVE DILUENTS AND WITH PHOTOINITIATOR IRGACURE 651

The use of high intensity radiation, and especially the ultraviolet (UV) to the process of polymerization and hardening of various kinds of monomers and oligomers provoked during the last twenty years a quantitative increase and the range of application in many an important technological branch of industry. Oligomers containing the highly reactive acrylic groups at both of their ends are mainly used in the industry. The materials hardened with the help of the UV radiation are used for example as protective coatings for metals, plastic materials, optical fibres, magnetic apparatus, as the materials in electrotechnics and in lithography^{1,2,3}. Our interest is connected with the application of diacrylates as the main components of the UV hardened compositions for the protective coatings of optical fibres.

In this report the results of research concerning synthesis of diacrylate and dimethylacrylate of diglycidyl ethers of Bisphenols: P(1,1-bis-(4-hydroxyphenyl)-cyclopentane), C(1,1-bis-(4-hydroxyphenyl)-cyclohexane), H(1,1-bis-(4-hydroxyphenyl)-cycloheptane) and also lacquer compositions made of these components are given. Glycidyl ethers were prepared in the reaction of bisphenols with epichlorohydrin in the two phase liquid/liquid system including the organic and aqueous phases. Estryfication of the above diglycidyl ether was carried out with the use of acrylic and methacrylic acid in the presence of TEBA (triethylbenzylammonium chloride) as a catalyst at the higher temperature. UV-curable compositions consist of the above mentioned acrylates, with reactive diluents and also with photopolymerization initiator 2,2-dimethoxy-2-phenyl-acetophenone (Irgacure 651) taken in amount of 2 percentage. Butyl acrylate, 2-ethylhexyl acrylate and styren were used as diluents.

For the obtained compositions there are determined: density, viscosity, index of refraction before curing, glass temperature, Young module, hardness, tensile strength, elongation and also thermal resistance after curing. It occurred that the properties of the investigated compositions are dependent on their structure and content. It was stated that the maximum resistance properties of the cured compositions as well as Young module were obtained with the content of about 10-30 percentage active diluent.



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P2.32.

URETHANE-ACRYLATES AS MAIN COMPONENTS OF LACQUERS FOR PROTECTIVE COATING OF SOME MATERIALS

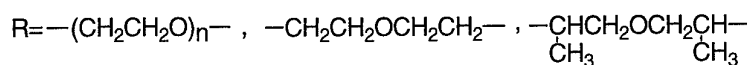
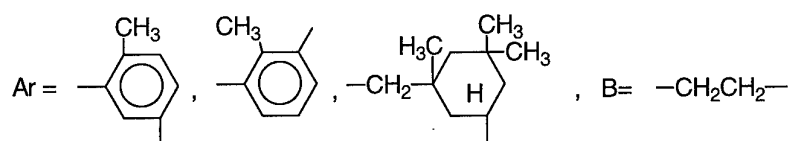
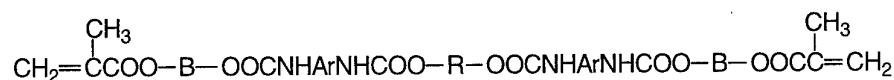
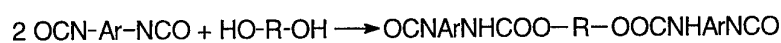
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THE SYNTHESIS OF URETHANE-ACRYLIC UV-CURED RESINS INTENDED FOR APPLICATION AS PROTECTIVE COATINGS FOR OPTICAL FIBRES

Oligomers containing the reactive acrylic groups at both ends are mainly used in industry. The materials used by UV radiation are used as protective coatings for metals, plastic materials, wood, as the materials in electrotechnics and lithography optical fibres¹⁻³.

During the last year our interest is concerned with synthesis and application oligourethane-acrylates as main components of the UV-cured compositions for the protective coatings of various materials and specially optical fibres⁴⁻⁶. A general scheme of the preparation of the urethane-acrylic oligomers is represented by the chemical reactions



In the first stage a molar excess of isocyanates: toluylene or isophorone with the glycols: oligooxypropylene M=2000, diethylene or dipropylene and an urethane prepolymer was obtained, containing some free isocyanate groups. Then in addition reaction with hydroxyethyl methacrylate it produced the urethane-acrylic oligomer. It was use the active

solvents: butyl acrylate, 2-ethylhexyl acrylate and 1,4-butanediol diacrylate, which decrease the viscosity as desired in accordance with the expectations and take part in the photopolymerization process of urethane-acrylate compositions. 2-Wt-%Irgacure 651 was added to the urethane-acrylates compositions as a photoinitiator. The urethane-acrylates compositions were exposed to the light of a Hg lamp (400 W, wavelength 320-380 nm) at a distance of 30 cm during 5 min. in non oxygen atmosphere.

The influence of the type and amount diisocyanates, glycols and active solvent on properties obtained oligourethane-acrylates was studied. It was shown, that the lacquer compositions obtained depending on their kind and quality may be used as three kinds of protective covers of optical fibres. Some mechanical properties for three kinds of covers are as follows. Soft cover: Young module - 1,9 MPa; hardness Shore'a A - 50; intermediate cover: Young module - 75 MPa, hardness Shore'a A - 80; hard cover: Young module 225 MPa, hardness Shore'a D - 75.

The applicability of the obtained compositions for protective coating of optical fibres was confirmed in the technological process which was carried out.

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P2.33.

QUALITY IMPROVEMENT OF SOL-GEL MULTILAYER ZIRCONIA COATINGS BY POLIMERIC ADDITIVE

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A improved dip-coating method of depositing zirconia thick multilayer coatings on glass from sol-gel solutions is described and the results have been discussed. Basic sol-gel solutions which comprise Zirconium propoxide, n-propanol, acetylacetone, water and a few drops of nitric acid, were stable for several months. However, coatings prepared on the base of these solutions have numerous defects such as crazing, cracking and pin-holing. It was found that the quality of thick films can be improved by adding polymeric additive PEG 200 to the sol-gel solution. The best ratio of Zirconium propoxide to PEG 200 was established. Prepared films have been characterized by Thermal Analysis (TA), x-ray. Diffraction (XRD), Scanning Electron Microscopy (SEM), Rutherford Backscattering Spectroscopy (RBS) and Scanning Auger Microprobe (SAM). The results of RBS and SAM give the rough estimation of the thickness of about 0.1 μm for one coating and the maximum value about 1 μm for several repeated dipping.

Last Minute Abstracts

Session 1

ENGINEERING PROPERTIES OF SPIDER SILK

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Strength and toughness are usually considered mutually exclusive properties for materials. In spite of the progress made in the recent years in polymeric fiber science and technologies, the search for a truly strong and tough fiber continues. It is of practical and scientific interest to explore the limit of strength and toughness of fibrous materials; and to examine the factors which contribute to the development of a combination of strength and toughness in materials. The answers to these questions may be found in nature.

In the world of natural fibers, spider silk has long been recognized as the wonder fiber for its unique combination of high strength and rupture elongation. An earlier study, as shown in Figure 1, indicated spider silk has strength as high as 1.75 GPa at a breaking elongation of over 26% [1]. With toughness more than three times that of aramid and industrial fibers, spider silk continues to attract the attention of fiber scientists and hobbyists alike.

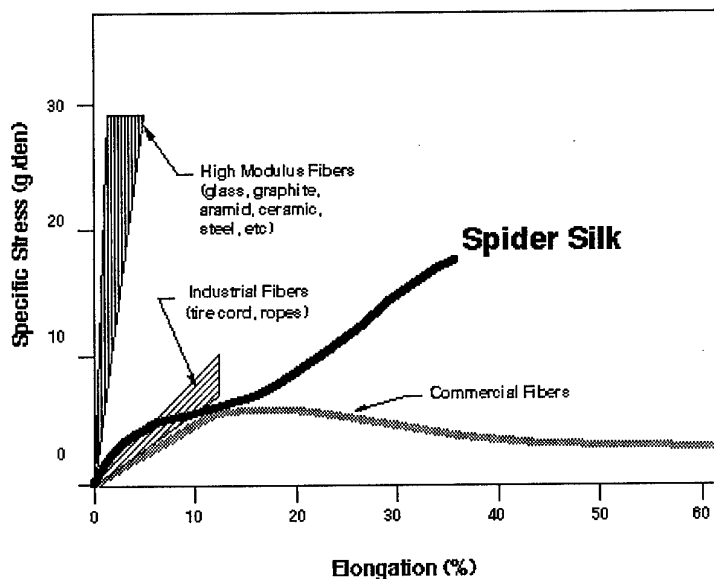


Figure 1. Tensile Stress-Strain Behavior of Agiope Aurentia Spider Silk

Considering the remarkable mechano-chemical properties of spider silk and fueled by the recent progress in biotechnology, there is a revival of interest in using spider silk as a model for the engineering of high energy absorption fibers [2]. Because of the fineness of spider silk, on the order of $4\mu\text{m}$, the characterization of the mechanical properties of spider silks are limited to tensile mode. Little is known about the response of spider silks to other modes of deformation in the transverse direction and in torsion. Original data are presented on the tensile, transverse compression and torsional stress-strain properties of the spider silk from *Nephila Clavipes* spiders. This was made possible by using an ultra sensitive micromasurement fiber testing system developed by Kawabata [3]. From these experimental data, the engineering properties: tensile modulus, transverse compressive modulus, and shear modulus of the spider silk was determined. It was founded that, as shown in Table 1, although the properties of the spider silks vary from species to species, they all have a high level of combined strength and toughness as well as shear resistance much greater than that of some of the toughest synthetic fibers such as the aramid fibers.

Table 1. Engineering properties of spider silk.

Tensile Modulus E_L (GPa)	Compressive Modulus E_T (GPa)	Shear Modulus G (GPa)
12.71 (25.6%)*	0.579 (41.3%)*	3.58 (19.7%)*

* Coefficient of Variation

This study demonstrated that spider silk is an excellent model for the development of strong and tough materials. With a highly anisotropic mechanical behavior, the sensitivity of the initial modulus and elongation but not ultimate strength to moisture indicated an interesting molecular composite structure composed of well ordered fibrillar structures oriented in a primitive helical structure.

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Session 2

**PREPARATION OF INTERFERENCE LAYER SYSTEMS AND
HOLOGRAPHIC PATTERNS ON GLASS AND PLASTIC
SUBSTRATES USING PHOTOPOLYMERIZABLE
NANOPARTICLES**

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A new synthesis and preparation route to interference layer systems and holographic patterns has been developed. It is based on oxide nanoparticles with high (TiO_2) and low (SiO_2) refractive index, which are synthesized by hydrolysis and condensation of appropriate alcoxides in presence of small amounts of functionalized silanes in alcoholic solution. These act as surface ligands for the stabilization of the particles and allow an interparticulate chemical bonding by UV polymerization of appropriate functional groups (methacrylate or epoxide). The nanoparticulate sols can be used for the deposition of optical (quarterwave) coatings on glass and plastics by dip-, spin- or spray-coating and subsequent UV-curing. In this way, multiple interference layer stacks of up to 7 single layers can be prepared and densified in a final step (stackfiring) on glass or plastics at temperatures of 450°C to 640°C and 80°C to 120°C respectively without damaging. The coatings exhibit excellent scratch hardness (comparable to the substrate glass or plastic respectively), UV and hydrolytic stability. TiO_2 coatings can also be used for the preparation of holographic micropatterns by embossing and UV curing. Due to the high refractive index ($n_D=1.93$ after UV curing) high diffraction efficiencies (for example of 28 % for a sinusoidal structure of 300 nm periodicity) can be obtained.

The high application potential of the new systems is demonstrated by a 5-layer NIR reflexion and a 3 layer antireflective filter on glass and plastics and by several holographic grating patterns on glass and plastics.

Session 2**NANOBINDERS FOR NATURAL COMPOSITES****Kalleder, A., Goedicke, S., Reinhard, B., Schmidt, S.**Institut für Neue Materialien gem. GmbH
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A new nanoparticulate binder has been synthesized for the fabrication of natural fiber composites with special properties. The binder consists of nano-scaled colloidal silica particles, whose surface is modified with organo alkoxy silanes in order to reduce the degree of condensation and to provide sufficient flexibility. On this basis a binder in form of a 35 weight % solution in ethanol with an average silica content of about 85 wt.% and 15 wt.% of organic groupings has been developed. Using this binder different types of natural fibers were bound, e.g. jute, hemp and straw. The water absorption of jute components fabricated with the new binder show a water take up of only 7 % compared to the untreated fibers (15 h arranged in 70 °C water). In case of stacks of straw with parallel arranged blades and 30 mm in thickness bound with the nanobinder, laminates with wooden panels 3 mm in thickness on both sides were prepared resulting in flame resistant construction elements with a compressive strength of 3.5 MPa by a specific weight of only 0.13 g/cm³.

These first results indicate the promising potential of natural fibers bound with a new type of inorganic binder prepared by wet chemistry. Further investigations will be carried out in order to meet individual demands.

*Session 2***HYDROTHERMAL SYNTHESIS OF NANOCRYSTALLINE
PERWOSKITE POWDER SYSTEMS**

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A chemical processing technique for the fabrication of nanopowders in the perovskite system has been developed. The route is based on the precipitation of amorphous precursors from aqueous or alcoholic solutions. The precipitation occurs in the presence of surface modifiers which prevent agglomeration during synthesis. After thermal treatment in an autoclave system at temperatures below 250 °C nanocrystalline powders were obtained. The powders are showing pure perovskite structure and primary particle size in the range of 10 nm in the case of BaTiO₃ and 50 - 100 nm in the case of PZT. Powders are showing redispersibility to the primary particle size.

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